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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
A.	Abstracts in Journal of the Chemical Society.*
Amer. J. Bot. . .	American Journal of Botany.
Amer. J. Pharm. .	American Journal of Pharmacy.
Amer. J. Sci. . .	American Journal of Science.
Analyst . . .	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. . .	Annales de Chimie.
Ann. Chim. anal. .	Annales de Chimie analytique appliquée à l'Industrie à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik . .	Annalen der Physik.
Ann. Physique . .	Annales de Physique.
Ann. Report . .	Annual Reports of the Chemical Society.
Annali Chim. Appl. .	Annali di Chimica Applicata.
Apoth. Zeit. . .	Apotheker-Zeitung.
Arch. ital. Biol. .	Archives italiennes de Biologie.
Arch. méd. exp. . .	Archives de médicine experimentale et d'anatomie pathologique.
Arch. Pharm . .	Archiv der Pharmazie.
Arkiv. Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J. . .	Astrophysical Journal.
Atti R. Accad. Lincei .	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. bot. Ges. .	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. physikal. Ges. .	Berichte der Deutschen physikalischen Gesellschaft.
Biochem. J. . .	The Biochemical Journal.
Biochem. Zeitsch. .	Biochemische Zeitschrift.
Boll. chim. farm. .	Bolletino chimico farmaceutico.
Bot. Gaz. . . .	Botanical Gazette.
Brit. Med. J. . .	British Medical Journal.
Brit. Pat. . . , .	British Patent.
Bull. Acad. Sci. Petrograd.	Bulletin de l'Academie Impériale des Sciences de Petrograd.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Jard. bot. Buitenzorg.	Bulletin du Jardin botanique de Buitenzorg.
Bull. Sci. Pharmacol. .	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim. .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
Centr. Min. • . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. and Met. Eng. .	Chemical and Metallurgical Engineering.
Chem. News . .	Chemical News.
Chem. Weekblad . .	Chemisch Weekblad.

* The year is not inserted in references to 1920.

Abbreviated Title.	Journal.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Naturforsch. Ges. Halle	Mitteilungen der Naturforschenden Gesellschaft zu Halle.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nachr. Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oesterr. Chem.-Zeit.	Oesterreichische Chemiker-Zeitung.
P.	Proceedings of the Chemical Society.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift
Proc. Amer. Inst. Electrical Engineers	Proceedings of the American Institute of Electrical Engineers.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Colorado Sci. Soc.	Proceedings of the Colorado Scientific Society.
Proc. Iowa Acad. Sci.	Proceedings of the Iowa Academy of Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Schweiz. Apoth. Zeit.	Schweizerische Apotheker Zeitung.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Soil Sci.	Soil Science.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
T.	Transactions of the Chemical Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Soc. Glass Technology	Transactions of the Society of Glass Technology.
U.S. Pat.	United States Patent.
Wien Anz.	Anzeiger der Akademie der Wissenschaften Mathematisch-Naturwissenschaftliche Klasse, Wien.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.

ABBREVIATED TITLE.	JOURNAL
Zeitsch. Nahr.-Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. Physik	Zeitschrift für Physik.
Zeitsch. physikal. Chem.	Zeitschrift fur physikalische Chemie, Stochiometrie und Verwandtschaftslehre
Zeitsch. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. Ver. deut. Zucker-ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE past year marks the attainment of the pre-war level so far as physical chemistry is concerned. In the new conditions which now obtain, however, this will certainly not represent the average output; a considerable increase may be anticipated in subsequent years, and compilations such as the present will almost certainly have to be expanded to keep pace with the advance.

A great deal of research has been carried out in the field of atomistics, and this is reflected in the present Report, unfortunately to the exclusion of much which should have found a place. It was felt, however, that just now a very limited number of those topics should be dealt with, which, to be understood, could not be treated except in some detail, so as to enable a return to be made eventually to a treatment presenting greater variety and probably, therefore, greater general interest.

Energetics of the Crystal Lattice.

The interest aroused in the problem of the structure of crystals by the pioneer work of Laue and the Braggs has led to an intensive study, in the first instance by Born and later by others, of the mechanics of the lattice, the energy involved in its dissociation into ions, its formation from the elements, and allied problems. The X-ray method has shown that, in general, the atom and not the molecule is the significant material unit. By a refinement of the X-ray method, P. Debye and P. Scherrer[1] have succeeded in showing that the electrons belonging to an atom are concentrated inside a very small space around the nucleus, the radius of the space being

[1] *Physikal. Zeitsch.*, 1918, **19**, 474 ; *A.*, 1919, ii, 20.

about one-tenth of δ, where δ is the so-called "lattice constant," and denotes the distance between two similar atoms. M. Born[2] has shown further that the atoms in salt crystals are electrically charged; they are, in fact, ions, carrying a charge identical with the charge of an electron in the case of salts of the type of potassium chloride. The properties of the crystal lattice involve a knowledge of the laws of electrical attraction and repulsion existing between any pair of oppositely-charged ions. It has been shown by Born that the attraction follows the ordinary inverse square law, whilst the repulsion varies as the inverse tenth power, or the potential of the repulsive force varies as the inverse ninth power of the distance. On this basis the compressibility of crystals of the cubic type can be accurately computed, as can also the lattice constant.[3]

The fact that the potential of the repulsive force involves an exponent $n = 9$ is of importance in connexion with the structure of atoms in general. Thus Born and Landé[4] have shown that the atomic model of Bohr (in which the electrons revolve in concentric orbits round the nucleus), when applied to crystals, gives rise to $n = 5$, which in turn leads to values for the compressibility which are approximately twice as great as those observed. The discrepancy is so great that in Born's opinion[5] it is necessary to discard the Bohr atomic model. He finds that the cubical atom model of G. N. Lewis leads to the required inverse ninth power relation in the case of crystals. This makes it almost certain that the cubic atom model with electrons moving in restricted or localised paths is in better accord with the facts than is Bohr's model, especially for those cases in which more than one electron is present in the atom. This conclusion will be referred to again in a subsequent section.

On the basis of the above laws of attraction and repulsion, Born[6] has developed the following expression for U, the energy required (strictly at absolute zero) to dissociate completely one gram-molecule of crystal lattice into free ions:

$$U = \frac{Na}{4\delta} \frac{n-1}{n}$$

where N is the Avogadro constant, δ the lattice constant, n the exponent of the potential of the repulsive force, and a is a constant characteristic of the attractive force (attractive force =

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[2] *Sitzungsber. Preuss. Akad. Wiss. Berlin,* 1918, 604; *A.,* ii, 401.

[3] M. Born and A. Landé, *Ber. Deut. physikal. Ges.,* 1918, **20,** 210; *A.,* 1919, ii, 188; M. Born, *Ann. Physik,* 1920, [iv], **61,** 87; *A.,* ii, 227.

[4] *Sitzungsber. Preuss. Akad. Wiss. Berlin,* 1918, 1048; *A.,* ii, 424; *Ber. Deut. physikal. Ges.,* 1918, **20,** 202; *A.,* 1919, ii, 188.

[5] *Ber. Deut. physikal. Ges.,* 1918, **20, 230;** *A.,* 1919, ii, 188.

[6] *Ibid.,* 1919, **21,** 13; *A.,* 1919, ii, 214.

a/δ^2). On the basis of this equation Born has calculated the value of U for a considerable number of salts. A few typical results are quoted to give an idea of the order of magnitude involved. The unit of energy is the kilo.-calorie.

Salt.	LiCl.	NaCl.	KCl.	RbCl.	CsCl.	KBr.	KI.
U	179	182	163	155	156	155	144

The accuracy of these values has been tested in an approximate manner by Born by considering a reaction of the type: [NaCl]+ [KI]=[KCl]+[NaI] (the square brackets denote the solid state), in which the net change in U can be equated to the net heat effect, the latter term being obtained by algebraic summation of the individual heats of formation of the salts from their elements. Unfortunately, the net heat effect and net change in U are very small quantities. So far as the comparison goes it is favourable to the lattice theory. Born has attempted to carry out an alternative test by taking into consideration the energy required to ionise the gaseous atoms of the elements from which the salt would ordinarily be formed—it is important to observe that U refers to formation of salt from the free ions and not from the atoms. The results obtained by this method also lend support to the lattice theory. A more exact test of the validity of the equation already given for U has been carried out,[7] based on the heat of solution of salts in water to form very dilute solutions. The results substantiate the theory in a satisfactory manner.

Fajans[8] has further investigated the heat of solution, L, of individual salts, pointing out that this quantity is composed of two effects, (a) the energy required to dissociate the salt into free gaseous ions, namely, U, and (b) the heat evolved when these ions are dissolved in water. The latter effect is regarded by Fajans as "heat of hydration of gaseous ions," the term hydration being taken to mean the condensation of an indefinite (non-stoicheiometric) number of water molecules around the ion as a result of electrostriction. Taking the case of potassium chloride we can write:

$$K^+_{gas} + Cl^-_{gas} = [KCl]_{solid} + U,$$
$$[KCl]_{solid} + aq. = K^+aq. + Cl^-aq. + L,$$

whence $\quad K^+_{gas} + Cl^{-+aq.}_{gas} = K^+aq. + Cl^-aq. + U + L.$
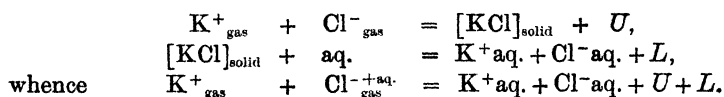
From this it follows that $W_{(cation)+(anion)}$, the heat of hydration of both ions, is given by:

$$W_{(cation)+(anion)} = U + L.$$

[7] K. Fajans, *Ber. Deut. physikal. Ges.*, 1919, **21**, 542; *A.*, ii, 21.

[8] *Ibid.*, 549; *A.*, ii, 12.

The following typical results indicate the extremely high, values obtained in this way. The heat of hydration is expressed in kilo.-cal. per gram-molecule.

Salt	LiCl.	NaCl.	KCl.	KBr.	KI.
$W_{(cation+anion)}$	187	180·5	159	150	139

The calculation just given affords values for the heat of hydration of both ions. The heat of hydration of individual ions has been calculated [9] by a method based on measurements of the refractive indices of aqueous solutions of alkali chlorides. The value obtained for the heat of hydration of the chlorine ion itself is 172 kilo.-cal. This is nearly the same as the values quoted above. That is, the cations have a negligible heat of hydration. This is a distinctly surprising result, and must be received with caution.

The next problem to which Born,[10] and later Fajans,[11] applied the lattice theory was the calculation of the affinity of neutral halogen atoms for electrons. This affinity is measured by E, where E is defined as the work which must be expended in removing an electron from a halogen ion. Born shows that E is a positive quantity, that is, the neutral halogen atom has a positive affinity for an electron. Born's argument is as follows. We begin with solid potassium chloride and imagine it decomposed into free gaseous ions in two different ways. The first way corresponds with the direct dissociation which involves an absorption of U energy units, 163 kilo.-cal. per gram-molecule. The second way corresponds with the decomposition of the salt into its electrically neutral elements, metallic potassium and gaseous molecular chlorine, whereby Q units are absorbed, namely, 106 kilo.-cal. The potassium is then vaporised, the heat absorbed being about 21 kilo.-cal., and the atoms are ionised into ions and free electrons. The latter process corresponds with the ionisation potential of the metallic vapour, namely, 99 kilo.-cal. At the same time, the molecular chlorine is dissociated into its atoms, the heat absorbed being 53 kilo.-cal. per gram-atom, and each of these atoms attaches to itself one of the electrons set free by the ionisation of the potassium vapour. We have thus arrived at the same end-point by two different paths. Equating the energy terms, it is found that the union of an electron with the chlorine, bromine, and iodine atom, respectively, involves the evolution of 116, 87, and 81 kilo.-cal. per gram-atom. No direct measurement of E is available. Born has tested the accuracy of the calculated value by an indirect method, based on

[9] F. Haber, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 990 ; *A.*, ii, 244.

[10] *Ber. Deut. physikal. Ges.*, 1919, **21**, 679 ; *A.*, ii, 156.

[11] *Ibid.*, 714 ; *A.*, ii, 156.

the ionisation of the hydrogen haloids. The mode of ionisation in this case was assumed by Born to be: $HCl \longrightarrow H^{\cdot} + Cl'$, and this assumption was later confirmed experimentally.[12] The corresponding energy term we shall denote by J_{HCl}. The various inter-relationships in the case of gaseous hydrogen chloride are conveniently shown by the following scheme, which is due to Haber[13]:

$$
\begin{array}{ccccc}
HCl & \longleftarrow & Q_{HCl} & \longleftarrow & H, Cl \\
\uparrow & & & & \uparrow \\
J_{HCl}^{\cdot} & & & & J_{H} \\
\uparrow & & & & \uparrow \\
H^{+}, Cl^{-} & \longleftarrow & E & \longleftarrow & H^{+}, Cl, e
\end{array}
$$
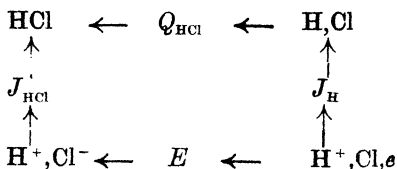
Symbols separated by commas indicate free atoms or ions separated by an infinite distance from one another. The direction of the arrows corresponds with an evolution of heat. Incidentally, the quantity J_{HCl} differs from U_{HCl} by an amount identical with the heat of sublimation of hydrogen chloride. Q_{HCl} denotes the heat which would be evolved by the union of atomic hydrogen and atomic chlorine, a quantity which is known to be 117 kilo.-cal. per gram-molecule of hydrogen chloride formed. J_{H} denotes the energy of ionisation of a free hydrogen atom, namely, 310 kilo.-cal. per gram-atom, or 13·4 volts. The symbol e stands for an electron. Passing from the right-hand lower corner of the scheme to the upper left hand by the two paths, and equating the energy terms, it is found that $J_{HCl} = 311$ kilo.-cals., this quantity being based in part on the value of E for chlorine calculated by the lattice theory. 311 Kilo.-cal. corresponds with an ionisation potential of 13·5 volts. Foote and Mohler[12] have found by direct experiment 14 volts. The agreement is satisfactory. It may be mentioned that Cuthbertson's value for the dispersional frequency of hydrogen chloride corresponds with $\lambda = 918·67$ Å. Converting this into frequency, and applying the quantum formulation, we find $Nh\nu = 309$ kilo.-cal., a value which is in very good agreement with that obtained by Foote and Mohler. It is noteworthy that the energy of ionisation of hydrogen chloride into two ions is practically the same as that required for the ionisation of the hydrogen atom into the hydrogen nucleus and a free electron. This means that the affinity of the hydrogen nucleus for an electron is practically the same as the affinity of the hydrogen nucleus for a halogen ion. This is considered in some detail by Haber,[13] who concludes that the heat of formation of all the alkali

[12] P. D. Foote and F. L. Mohler, *J. Amer. Chem. Soc.*, 1920, **42**, 1832; *A.*, ii, 660.
[13] *Ber. Deut. physikal. Ges.*, 1919, **21**, 754; *A.*, ii, 156.

chlorides in the gaseous state from the gaseous atomic elements is the same as that for hydrogen chloride, namely, 117 kilo.-cal. per gram-molecule of salt. In the course of Haber's considerations, he estimates that the heat of sublimation of the alkali haloids is of the order 60 kilo.-cal., a very large quantity when compared with the corresponding term for the solid hydrogen haloids, namely, 4 to 5 kilo.-cal. Haber shows that the above value for the heat of sublimation of the salts is in agreement with their high sublimation temperature. Further, the heat of sublimation of the alkali chlorides has been calculated to be about 50 kilo.-cal.[14] Haber has succeeded in verifying his value for the heat of sublimation by an alternative mode of calculation, making use of a scheme analogous to that already employed in connexion with gaseous hydrogen chloride.

In the foregoing considerations, the hydrogen chloride appears as a gas, and the energy term J_{HCl} refers to this state. Reis[15] has put forward certain important considerations in connexion with the lattice of the crystalline hydrogen haloids. He points out the low heat of sublimation as compared with that of the alkali haloids, and also the extremely high energy of ionisation (300—320 kilo.-cal.), which is about twice as great as that of the alkali haloids (150—180 kilo.-cal.). He also points out the relatively large molecular volume of the solid hydrogen haloids, and finally concludes that the lattice in these cases must be very different from the lattice in the case of the salts. This difference he attributes, very reasonably, to the existence of molecules, as distinct from ions, as the significant material units composing the lattice in the case of the solid hydrogen haloids. He confirms this view by a consideration of the electric moment of the hydrogen chloride molecule.

Returning to the alkali haloid (ionic) lattice it may be pointed out that Haber has applied the quantum theory to this case in the following ingenious manner. Haber regards the known dispersional frequency v_0 of the solid salt, obtained from measurements of the refractive index, as representing the most violent electronic movement of which the lattice is capable, and therefore corresponding probably with the energy U required for its ionisation. We can thus write $U = Nhv_0$, where N is the Avogadro constant and h is Planck's constant. In the case of potassium chloride (sylvine), the limiting wave-length λ_0, which corresponds with v_0, has been found to be $160 \cdot 7 \mu\mu$, λ_0 for rock-salt being

[14] A. Reis, Zeitsch. Physik, 1920, 1, 204 ; A., ii, 537.
[15] Zeitsch. Elektrochem., 1920, 26, 408 ; Zeitsch. Physik, 1920, 1, 299 ; A., ii, 751.

156·3 $\mu\mu$. Hence $Nh\nu_0$ for potassium chloride and for sodium chloride is calculated to be 177 and 182 kilo.-cal. respectively, whilst U, as calculated by Born, is 163 and 182 kilo.-cal. respectively. The agreement is striking. In the case of other salts for which Born has calculated U, the necessary refractive index measurements have not been made. Haber, however, makes use of his "square root rule," which connects the known characteristic infra-red vibration frequency of a salt, as determined by Rubens, with the quantity ν_0, and thus calculates approximate values for $Nh\nu_0$, which are compared with U in the following table:

Salt	NaCl.	KCl.	KBr.	KI.	TlCl.	TlBr.	TlI.	LiF.
$Nh\nu_0$ kilo.-cal.	173	165	151	141	144	157	142	336
$U_{Born.}$, kilo.-cal.	182	163	155	144	169	163	151	231

With the exception of lithium fluoride, where the discrepancy is enormous, the agreement is fairly satisfactory. The calculation serves to link up the frequency of the dispersional electron with the properties of the crystal lattice.

We now pass from a consideration of salts to a consideration of metals. Metals are characterised by their thermal and electrical conducting capacity, properties which were formerly explained on the basis of freely moving electrons, each of which possessed considerable thermal capacity. The determinations of the specific heats of metals, carried out in great detail to test the applicability of the quantum theory, have shown, however, that the heat capacity of electrons is negligible until extremely high temperatures are reached. The free electron theory therefore breaks down. In its place, F. A. Lindemann [16] suggested, several years ago, that a metal consists of two interleaved space lattices, one consisting of metallic ions, the other of electrons. On this basis, the electrical conductivity is due to the movement of the electron lattice as a whole through the ionic lattice. The resistance which the electron lattice experiences is due to vibrations of the ions, which impede the movement of the electron lattice as a result of electrical repulsions. At very low temperatures, however, the vibrations of the ions are small, and the electrical conductivity should be abnormally great. This corresponds with the known supra-conductive state discovered by Onnes at the temperature range 3° to 0° absolute. If the metal is not pure, the ionic lattice is heterogeneous, and the electron lattice has greater difficulty in moving through it. That is, the presence of an impurity should increase the resistance of a metal, a conclusion which is borne out by

[16] *Phil. Mag.*, 1915, [vi], **29**, 127 ; *A.*, 1915, ii, 47.

experiment.   As the electron lattice moves through the ionic lattice at temperatures above zero, it will transfer to the latter a certain amount of the kinetic energy it has gained from the impressed electric field; in other words, the temperature of the metal will rise as a consequence of the passage of current.   Lindemann shows, further, that the lattice theory of the metallic state is in agreement with Ohm's law.   As regards thermal conductivity, on the lattice theory heat is transmitted by elastic waves.   The thermal conductivity of a metal may be regarded as the sum of the conductivities of the two lattices.   The thermal conductivity of the ionic lattice is necessarily of the same order as that of a salt crystal, and is therefore negligible at ordinary temperatures. The conductivity of the electron lattice, on the other hand, will be large, for as Lindemann shows, it will behave like an ionic lattice when the latter is at very low temperature, when such lattices are known to possess high thermal conductivity.   Further, the specific heat of the electron lattice, owing to its high limiting frequency, is extremely small.   Thus, without attributing any measurable heat capacity to the electrons, it is possible to have large thermal conductivity as a whole in the case of a metal.   This is in excellent agreement with the results obtained from measurements of specific heats, and constitutes the main advantage of the electron lattice theory, as distinct from the older free electron theory.   Lindemann shows, further, that the lattice theory is capable of explaining the mechanism of the photo-electric effect, even accounting for the difficulty that the energy of the photoelectron is often greater than the incident energy of the light falling on one electron.   On the lattice theory, a large part of the wave-front can act on the electron lattice, setting up an elastic wave sufficiently intense to eject an electron from the lattice.

A lattice theory of metals has also been worked out in some detail by Haber,[17] based directly on Born's concepts.   The lattice in this case consists, of course, of ions and electrons.   Using Born's theory, an expression for U, the lattice energy, can be calculated in terms of the compressibility and atomic volume of the metal. Haber also points out that U can be equated to $D + J_m$, where D is the known heat of sublimation of the metal and J_m the energy of ionisation of the vapour, corresponding with the well-known ionisation potential of the latter.   The agreement between the two modes of calculating U is apparently satisfactory.   The following typical values, expressed in kilo.-cal. per gram-atom, indicate

[17] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 506, 990; *A.*, ii, 424.

that the lattice energy of a metal is of quite the same order of magnitude as that of the haloid salts:

Metal	Li.	Na.	K.	Rb.	Cs.	Ag.	Tl.
U	155	140	123	117	109	243	206

From the values of U it should be possible to calculate, on the basis of Born's lattice theory, the value of the exponent n in the potential of the repulsive force. We have already seen that in the case of most salts $n = 9$. Haber finds in the case of the alkali metals that n lies between 2 and 4.

This raises a considerable difficulty, for, as Born has shown, such a value for n would mean that the electrons, instead of being fixed, would be free. To overcome this difficulty, Haber, making use of certain results obtained by Debye, substitutes a movable lattice in place of a statical one, and on this basis works out a number of relations. The problem does not seem, however, to be by any means satisfactorily solved, and as much of it is still speculative, we need not enter into it further here. What seems certain is that a lattice of some kind forms the basis of the metallic state.

The Crystal Lattice and Molecular Magnetic Fields.

In the foregoing section an account has been given of the crystal lattice, the material units of which are ionic, from the point of view of electrostatics. In the present section we review briefly the treatment of the crystal lattice, the material units of which are molecules from the point of view of magnetic forces.

That two electrons rotating in a certain manner with respect to one another will attract or repel with a force varying more rapidly than the inverse square of the distance has long been known. Since the introduction of the idea of moving electrons into atomic and molecular theory, the possibility of such electromagnetic attraction and repulsion playing an important part in chemical change has been recognised. This has been specially emphasised by E. C. C. Baly,[18] who has recently "quantumised" it in the molecular phase hypothesis, a concept also expressed in Bohr's theory of stationary states.

The problem with which we are more immediately concerned is the extent to which magnetic forces enter into and define the behaviour of crystalline substances. This has been investigated by A. E. Oxley,[19] mainly for the case of diamagnetic organic sub-

[18] *Phil. Mag.*, 1920, [vi], **40**, 15 ; *A.*, ii, 460.
[19] *Phil. Trans.*, 1914, [A], **214**, 109 ; 1915, [A], **215**, 79 ; 1920, [A], **220**, 247 ; *A.*, 1914, ii, 424 ; 1915, ii, 219 ; 1920, ii, 351.

stances in which the molecule, not the ion, is regarded as the significant material unit. Oxley's chief contribution to the subject consists in the demonstration that the local molecular field in a diamagnetic substance is comparable in magnitude with the ferromagnetic molecular field, being of the order 10^7 gauss. That this is a field of extremely high intensity is evident when we recall that the most intense field which can be produced artificially is of the order 10^4 gauss. The principal experimental evidence advanced by Oxley is the change in the specific diamagnetic susceptibility (measured in the case of about fifty substances) which accompanies the change from the liquid to the solid state.

On Langevin's theory of magnetism, the molecule of a diamagnetic substance contains oppositely spinning systems of electrons, which counterbalance one another externally, so that the molecule as a whole possesses no initial magnetic moment. When an external magnetic field is applied, the frequency of rotation of one electronic system is increased, whilst the other is diminished, and the molecule becomes slightly polarised and distorted. This small differential effect accounts for the well-known Zeeman effect, and is also the origin of the small magnetic moment possessed by a diamagnetic substance when subjected to a magnetic field. The act of crystallisation can also be regarded as bringing about a similar distortion of the molecule, so that the difference in susceptibility of the solid and liquid forms may be employed to determine the order of magnitude of the local field of magnetic molecular force which gives rise to the rigidity characteristic of the crystalline form.

Let us suppose that ΔM is the change in the moment, M, of an electron orbit produced by applying a magnetic field, H, τ being the period of rotation of the electron (of the order 10^{-15} sec.) and e/m the ratio of the charge to the mass of an electron. Langevin has shown that

$$\frac{\Delta M}{M} = -\frac{H\tau e}{4\pi m} = 10^{-9} \cdot H$$

The strongest magnetic field which can be produced artificially being of the order 10^4 gauss, the largest value of ΔM is $10^{-5}M$. Suppose, however, that, as a result of crystallisation, the molecular field produced is of the order 10^7 gauss, then the value of ΔM is 10^{-2}, which would mean a change of 1 per cent. in the susceptibility. This is the order of the change observed in the case of aromatic compounds. Other evidence confirming the extremely high value ascribed to the molecular field is furnished by the results obtained with double refraction, magneto-striction,

and magneto-rotation. Thus, when a liquid is brought into a magnetic field, it becomes slightly doubly refracting, and at the same time undergoes a small diminution in volume. Oxley shows that if a field of 10^7 gauss could be applied (this being the field which is supposed to be produced by crystallisation), a double-refraction comparable with that exhibited by quartz would be produced. Under the same field, the decrease in volume would be about 10 per cent., a value in good agreement with the observed change in volume on crystallisation in numerous cases.

It must be emphasised that, on the view expressed above, the molecule of a diamagnetic substance is locally ferro-magnetic, that is, one part of the molecule is a north-seeking, the other part a south-seeking, pole; this is regarded as the origin of molecular union. The repulsion observed when a diamagnetic substance is placed in a magnetic field is looked upon as purely an induction effect produced in a system of molecules, each of which has initially a zero magnetic moment.

Having considered the intensity, H_c, of the local molecular field, we have now to consider its energy. Let I denote the aggregate local intensity of magnetisation for all the molecules, n, in unit volume. Then $I = ni$, where i is the local magnetic moment of a single molecule. The potential energy E of 1 gram of the substance, in virtue of the grouping and distortion of the molecules constituting the crystalline form (that is, over and above the energy associated with 1 gram of the liquid) is then given by: $E = H_c I / 2\rho$, where ρ is the density of the crystal. If we assume that H_c is proportional to I, we can write $H_c = a'_c I$, where a'_c is a constant which Oxley shows is the reciprocal of the limiting local susceptibility of the crystalline medium under a field strength identical with that possessed by the molecular field itself. The energy E can therefore be written as $a'_c I^2 / 2\rho$, which is analogous to the expression $NI^2/2\rho$ obtained by Weiss for ferro-magnetic substances. The constant a'_c corresponds with N, both having the same physical significance for the respective kind of substance. Oxley shows that the numerical values of a'_c and N are comparable, as are also the I terms, so that the energy of the molecular field in the case of a diamagnetic, crystalline substance is of the same order of magnitude as that of a ferro-magnetic solid, namely, 10^9 ergs per gram. Now in the act of fusion the crystalline form is destroyed; the latent heat of fusion should therefore be of the order $10^9/4 \cdot 2 \times 10^7$, or 25 cal. per gram. The following are a few experimental values:

Benzene .... 30 cal.　Chlorobenzene... 30 cal.　Aniline .... 21 cal.
Nitrobenzene ... 22 ,,　Naphthalene ... 35 ,,　Pyridine .... 22 ,,

Reference must also be made to the variation in the specific heat

2 B*

of a crystalline solid as the melting temperature is approached. "In the crystalline state we must regard the molecules as orientated into definite positions with respect to their neighbours by these large intermolecular forces. If at the higher temperatures the molecules undergo rotational vibrations about their mean positions, then it would be expected that the value of I^2 would be somewhat lessened by these vibrations, and we should therefore expect that a small fraction of the energy associated with the grouping would be dissipated as the temperature is raised towards the fusion point. The effect this would have on the variation of the specific heat with temperature would be to add to the normal variation (expressed by Debye's theory) the following positive term:

$$\frac{a'_c}{2\rho J} \cdot I \cdot \frac{\delta I}{\delta T},$$

where T is the absolute temperature and J the mechanical equivalent of the calorie." Nernst and Lindemann have found that close to the melting point there is an abnormal increase in the specific heat of diamagnetic substances, and in order to account for this on the above basis it is necessary to give to I a large value, such as that required by previous considerations. It is necessary to point out that only a small fraction of the energy term E will be dissipated below the fusion point, the major part of it being involved in the act of fusion itself.

Again, the frequency v of the rotating electrons is given by:

$$v = He/2\pi m.$$

If the value ascribed to H be of the order 10^7 gauss, then v is of the right order of magnitude for an optical frequency. If inside a molecule the intensity were 10^9 gauss, frequencies corresponding with X-rays would be accounted for.

Finally, the intermolecular magnetic field will determine the tensile strength of the crystal, and, as the stresses will be different in general in different directions, planes of cleavage will occur. In this connexion it is important to recall the experiments of Tyndall, who found that the cleavages of diamagnetic substances when placed in a magnetic field stand equatorial, whilst the cleavages of magnetic substances stand axial. Oxley finds in this further evidence that the forces which produce crystallisation are magnetic in nature.

The precise relationship between the electrostatic theory of atomic and molecular forces as the basis of the crystal lattice and the magnetic theory of the lattice has not as yet been clearly defined. The measure of success which has attended both modes of treatment suggests that they are not mutually contradictory,

although at the present time it is impossible to say more than that in crystals of salts and possibly metals (ionic lattices) the electrostatic forces predominate, whilst in crystals of organic substances (molecular lattices) the intermolecular forces are essentially magnetic.

Ionisation and Resonance Potentials in Gases.

Two types of inelastic encounter between electrons and gaseous atoms are known. One of these in the simplest conditions results in the emission of a single frequency, without ionisation of the gas, whilst the other ionises the gas and causes it to emit a complete spectrum. The potential giving the first kind of encounter is called a resonance potential, that giving the second an ionisation potential. Both types of potential manifest themselves also in connexion with molecules. Thus the process of dissociation of a diatomic gas into neutral atoms would conceivably correspond with the lowest possible resonance potential characteristic of a gas. The importance of measuring such potentials lies in the fact that they afford information regarding the stability of molecules and atoms. We shall consider a number of gases in turn.

Hydrogen.—A very careful investigation of the behaviour of this gas has been carried out,[20] with the following results:

First, there is a weak but appreciable ionisation of the gas at $11 \cdot 5 \pm 0 \cdot 7$ volts. This is ascribed to the ionisation of the molecule, thus: $H_2 \longrightarrow H_2^+ + \ominus$ In support of this view it is pointed out that the ion formed at this potential is of molecular and not of atomic dimensions, thereby eliminating the possibility of ascribing the effect to $H \longrightarrow H^{\cdot} + \ominus$, which might be expected to occur at a higher potential. The conclusion drawn in connexion with the potential referred to is a serious criticism of Bohr's theory of the hydrogen molecule, for, according to this theory, the positively charged hydrogen molecule should be incapable of existence. J. J. Thomson, however, has shown that this individual exists in the canal rays.

Secondly, a resonance potential is found at $13 \cdot 6 \pm 0 \cdot 7$ volts. This is ascribed to the dissociation of the molecule into atoms, one of which is normal; the other contains two quanta. The latter emits the first line of the Lyman series in the far ultra-violet. This potential is written by the authors as $(10 \cdot 1 + Q)$ volt, where $Q = 3 \cdot 53 \pm 0 \cdot 25$ volts. This term will be considered later.

Thirdly, a strong ionisation has been observed at $17 \cdot 1 \pm 0 \cdot 27$ volts,

[20] J. Franck, P. Knipping, and T. Krüger, *Ber. Deut. physikal. Ges.*, 1919, **21**, 728 ; *A.*, ii, 145.

which is written as $(13\cdot5 + Q)$ volts. This is regarded as the ionisation of the hydrogen molecule into an atom, a nucleus, and a free electron, thus: $H_2 \longrightarrow H + H^{\bullet} + \ominus$.

Finally, a new ionisation stage has been observed at the very high voltage $30\cdot4 \pm 0\cdot5$, which is written as $(2 \times 13\cdot5 + Q)$ volts, and corresponds with the most violent change of which the neutral molecule is capable, namely, its ionisation into two nuclei and two free electrons: $H_2 \longrightarrow 2H^{\bullet} + 2 \ominus$.

The quantity Q (3·53 volts), which occurs in at least three of the observed stages, is ascribed to the dissociation of the hydrogen molecule into neutral atoms. As evidence of the general correctness of this view it is pointed out that 3·53 volts would correspond with 81,300 cal. per gram-molecule of hydrogen, a quantity which agrees fairly well with the heat of dissociation of the gas, 85,000 cals. as determined by Langmuir. This resonance potential was not observed directly by the authors named, although presumably it was looked for. It is of interest in this connexion to note that Mohler and Foote[21] obtained "evidence of a slight resonance collision between 2·5 and 3·5 volts, but the value has not yet been accurately fixed." It may perhaps be pointed out that by subtracting stage 3 from the final stage referred to we obtain the value 13·3 volts as the ionisation potential of the hydrogen atom, namely, $H \longrightarrow H^{\bullet} + \ominus$.

Values differing apparently from those of Franck, Knipping, and Krüger have been obtained by other workers. Thus, Franck and Hertz, Bishop, Davis and Goucher, found somewhat earlier that ionisation sets in at a potential of about 11 volts, and the latter authors further found a second ionisation potential at 15·8 volts. This value, which does not find any counterpart in the work of Franck, Knipping, and Krüger, is accounted for by assuming that the hydrogen atom has an affinity for an electron, so that the energy of decomposing the negatively charged ion, according to the scheme $H' \longrightarrow H + \ominus$, is 2·2 volts, where $2\cdot2 = (15\cdot8 - 13\cdot6)$ volts.

Hydrogen has also been carefully investigated,[22] with the following results:

First, there is a radiation or resonance potential at a minimum electron velocity equivalent to 10·5 volts. This is presumably the same as the 10·1 volts inferred by Franck and his collaborators as a possible resonance potential of the molecule. Horton ascribes this effect to radiation from the atom by displacement of an electron from one orbit to another.

[21] *J. Opt. Soc. Amer.*, 1920, **4**, 49 ; *A.*, ii, 464,

[22] F. Horton and (Miss) A. C. Davies, *Proc. Roy. Soc.*, 1920, [A], **97**, 23 ; *A.*, ii, 215.
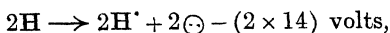
Secondly, a further type of radiation potential is produced at 13·9 volts. Horton ascribes this to radiation from the molecule. This is presumably the same as the resonance potential observed by Franck and his co-workers at 13·6 volts.

Thirdly, Horton and Miss Davies find that ionisation of the gas occurs at 14·4 volts. This value does not appear to correspond with any found by the other workers. It is rather a striking fact, however, that 14·4 volts corresponds with the wave-length 84 $\mu\mu$, which lies very near to the accepted value of the dispersional wave-length, 86 to 87 $\mu\mu$, obtained from refractive index data. Horton ascribes this stage to the ionisation of the atom $H \longrightarrow H^{\cdot} + \ominus$ It will be recalled that the value calculated for this process on Franck's data is 13·3 volts, which agrees well with the value calculated by Bohr.
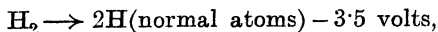
Finally, Mohler and Foote [21] find a resonance potential at 10·4 volts, which agrees very well with the first stage observed by Horton and Miss Davies. Mohler and Foote also find a first ionisation stage at 13·3 volts, which they ascribe to ionisation of the atom, in excellent agreement with the value calculated above. These authors also find a second ionisation at 16·5 volts, which they ascribe to the molecule. This evidently is intended to correspond with the value 17·1 volts found by Franck and his co-workers.

On the whole, the various observations are rather discordant. Something like order may be obtained from the various results if we take as our starting point the value 3·5 volts or 81,300 cal. for the dissociation of the molecule into neutral atoms, and assume that the various stages are approximately even multiples of this quantity. The various potentials and the corresponding wave-lengths calculated on this basis are compared with the observed values in the table on p. 16.
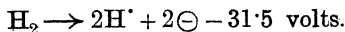
These various stages are logically connected with one another. For example, stage (6) follows from stages (1) and (4). Thus, from process (4) we have:

$$2H \longrightarrow 2H^{\cdot} + 2\odot - (2 \times 14) \text{ volts,}$$

and from (1):

$$H_2 \longrightarrow 2H(\text{normal atoms}) - 3\cdot5 \text{ volts,}$$

whence

$$H_2 \longrightarrow 2H^{\cdot} + 2\ominus - 31\cdot5 \text{ volts.}$$

Stage (6) would appear to be the highest possible stage of activation of which the neutral molecule is capable. The corresponding wave-length is much shorter than the limit ascribed to the hydrogen spectrum by Richardson and Bazzoni. It is obvious that the potentials of hydrogen require further exact investigation.

Process number.	Nature of process.	Potential calculated, volts.	Wave-length in $\mu\mu$.	Potential observed.
1.	$H_2 \longrightarrow 2H$. Both atoms normal. Resonance.	$3·5 = (3·5 \times 1)$	348	2·5 to 3·5
2.	$H_2 \longrightarrow 2H$. One atom normal, the others with displaced electron. Resonance.	$7·0 = (3·5 \times 2)$	174	not observed
3.	$H_2 \longrightarrow 2H$. Both atoms with displaced electrons. Resonance.	$10·5 = (3·5 \times 3)$	116	10·1 / 10·4 / 10·5
4.	$H \longrightarrow H^· + \ominus$. Ionisation of the atom.	$14·0 = (3·5 \times 4)$	87 (dispersional wave-length)	13·3 / 14·4
5.	$H_2 \longrightarrow H + H^· + \ominus$. Ionisation of the molecule. The atom is normal.	$17·5 = (3·5 \times 5)$	69·6	16·5 / 16·9 / 17·1
6.	$H_2 \longrightarrow 2H^· + 2\ominus$. Complete ionisation of the molecule.	$31·5 = (3·5 \times 9)$	38·7	30·4

Nitrogen.—The relatively early experiments of Franck and Hertz led to the value 7·5 volts as the ionisation potential of nitrogen. In view of the great chemical stability of the molecule this value is surprisingly low. B. Davis and F. S. Goucher[23] showed later that this potential did not give rise to ionisation, but to resonance. They found a more intense type of resonance potential at 9 volts and a true ionisation at about 18 volts.   H. D. Smyth[24] has investigated the values of the lower potentials with the following results:

First, there is a marked production of radiation (resonance) at $8·29 \pm 0·04$ volts. Secondly, there is a doubtful effect which he considers may be due to silicon at 7·3 volts; and thirdly, an effect at 6·29 volts, which only appears at low pressures, and which he finally attributes to nitrous oxide as an impurity. Smyth has also obtained qualitative evidence in support of Davis and Goucher's value, 18 volts, for the ionisation potential. Smyth concludes that the resonance potential at 8·29 volts corresponds with the dissociation of the nitrogen molecule into neutral atoms. The effective wave-length is therefore 149 $\mu\mu$, and the heat of dissociation per gram-molecule 190,000 cal. Mohler and Foote[21] confirm the general correctness of previous determinations by finding a resonance potential at $8·18 \pm 0·10$ volts and an ionisation potential at $16·9 \pm 0·5$ volts.

Oxygen.—The value hitherto accepted for the ionisation potential of this gas has been about 9 volts. Mohler and Foote[21] have carried out a careful revision, and find a/ resonance potential at

[23] *Physical Rev.*, 1919, **13**, 1.   [24] *Ibid.*, 1919, **14**, 409 ; *A.*, ii, 523.

7.91 ± 0.1 volts, which corresponds with the known wave-length 1570 Å. They also find an ionisation potential at 15.5 ± 0.5 volts, which agrees fairly well with the potential 15·2 volts calculated from the dispersional frequency of oxygen. It might be suggested that the value 9 volts corresponds with the process $O_2 \longrightarrow O_2^{\cdot} + \ominus$ analogous to the hydrogen potential 11·5 volts, $H_2 \longrightarrow H_2^{\cdot} + \ominus$, which lies between the resonance and true ionisation potential of this gas.

Iodine Vapour.—The behaviour of iodine vapour in respect of fluorescence, ionisation, and dissociation into neutral atoms has been examined by K. T. Compton and H. D. Smyth.[25] They point out that the fluorescence of gases and vapours is not generally accompanied by ionisation, and that therefore fluorescence is due to a shift of an electron from a position of high to one of low potential energy, a view first expressed in somewhat general terms by Baly as an alteration in the degree of openness of the molecular field of force. Compton and Smyth have obtained experimental evidence of the correctness of this view from measurements of the minimum energy required to ionise a fluorescing molecule. The normal molecule requires 10 volts, the fluorescing molecule 7·5 volts when excited by the green mercury line. The difference, 2·5 volts, corresponds with the quantum of energy of the mercury line as calculated by the relation $Ve = h\nu$. This result is direct experimental evidence of the existence of molecules with an abnormal energy content; such molecules are, in fact, partly active in respect of ionisation. Turning to the relationship between ionisation and dissociation into atoms, Compton and Smyth find two types of ionisation in iodine vapour, namely, a very weak ionisation at 8·5 volts, which they attribute to the ionisation of the free iodine atoms (formed in sensible quantity by contact with the hot filament), and also a very intense ionisation at 10 volts attributed to the molecules. The difference, 1·5 volts, should correspond with the energy required to dissociate a molecule of iodine into neutral atoms. This value, when converted into cals per gram-molecule, agrees closely with the known heat of dissociation. This result, it may be pointed out, also substantiates the view that the nascent atoms require no energy of activation in respect of their recombination. The wave-length corresponding with the above voltage (1·5) is about 820 $\mu\mu$. Iodine vapour would therefore be expected to exhibit an absorption band in this region; it does not appear to have been looked for hitherto.

Helium.—The potentials of this gas will be considered in the next section.

Neon.—The minimum radiation (resonance) potential has been

[25] *Science*, 1920, **51**, 571 ; *A.*, ii, 723.

found [26] to be 11·8 volts, the minimum ionisation potential 16·7 volts. A second resonance potential has also been found at 17·8 volts, and a second and third ionisation potential at 20·0 and 22·8 volts respectively. The existence of three ionisation potentials and two critical resonance potentials indicates that neon differs more from helium and argon than would have been anticipated. On the usual view the resonance and ionisation potentials correspond respectively with the lowest and highest frequencies of some particular series. It would be expected, therefore, that there should be as many resonance potentials as there are ionisation values. The fact that only two resonance potentials were found in this gas is ascribed to the possibility that two lie very close together, in which case one might escape detection. Another possibility is that the ionisation observed at one of the three potentials is a spurious effect. The resonance potential, 11·8 volts, appears to be associated with the ionisation potential, 16·7 volts, and the resonance potential at 17 8 volts with the ionisation at 22·8 volts. If neon consists of two or more constituents having different radiation and ionisation potentials, the critical potentials, 11·8 and 16·7, are attributed to one isotope, the values 17·8 and 22·8 to the other.

Argon.—Horton and Miss Davies [27] have also investigated this gas very carefully. Their final conclusions are that argon exhibits a resonance potential at 11·5 volts and an ionisation potential at 15·1 volts. The latter corresponds with the wave-length 817 Å. Lyman has found that the limiting wave-length of the argon spectrum lies very close to 800 Å. The agreement between the two results is satisfactory.

As regards the resonance and ionisation potentials of metallic vapours, a considerable amount of research has been carried out. One of the chief difficulties is that of the minimum arcing potential and the potential required to maintain the arc. In general, it may be said that the ionisation potential corresponds with the convergence frequency of a series, which, however, is not necessarily the principal series. Another point in dispute is as to whether the resonance potential corresponds with a single line or not. Until more general agreement is attained among the workers in this field as to the interpretation of their results there is little advantage in attempting to summarise them.

Before leaving the subject of ionisation of gases it may be pointed out that in the case of diatomic molecules two distinct types of ionisation may be expected. In the first the molecule parts with an electron, but preserves its general molecular structure. This is

[26] F. Horton and (Miss) A. C. Davies, *Proc. Roy. Soc.*, 1920, [A], **98**, 124; *A.*, ii, 657.   [27] *Ibid.*, **97**, 1; *A.*, ii, 215.

the type of ionisation met with in the diatomic gases referred to above. "It seems probable that materials capable of ionising in this manner should possess a characteristic spectrum." [28]   In the second type of ionisation the molecule breaks up directly into a positive and a negative ion. (Naturally, the first type of ionisation, in so far as it affects atoms, will ultimately, in certain cases, give rise to the same end-products as those obtained in a single step during the second type of ionisation.)   The second type of ionisation is met with in the case of hydrogen chloride, already discussed in the first section of this Report.   "Materials which are ionised in this manner probably do not possess characteristic spectra in the ordinary sense," beyond the line in the far ultra-violet corresponding with the union of the two ions.   It may be anticipated that the alkali haloids in the state of vapour exhibit the second type of ionisation.   This would explain the known absence of any emission spectrum characteristic of the salt.   We would expect instead to observe the spectrum of the alkali metal produced by a recombination of the metallic ions with electrons.   Further, the flame emission spectrum characteristic of the metals is suppressed by an excess of halogen.   This finds a simple explanation on the basis that the excess of halogen in the flame ultimately gives rise to halogen ions in relatively large amount with which the metallic ions combine rather than with the electrons.

The Atomic Model of Bohr and the Structure of the Helium Atom.

One of the main objections to Bohr's theory of the structure of a molecule such as that of hydrogen is that it requires the hydrogen molecule to be paramagnetic, whilst it is, in fact, diamagnetic.   An attempt has been made [29] to reconcile Bohr's theory with the actual diamagnetism of hydrogen on the basis of rotations and vibrations as well as of translatory movement of the molecule, so that although the structure is inherently paramagnetic the gas would behave as though diamagnetic.   The plausibility of this explanation has been adversely criticised by Oxley [30] in the light of recent experimental data, and the conclusion is drawn that thermal oscillations and rotations have little to do with the origin of diamagnetism, and that, in fact, the Bohr model for the molecule is incorrect.   Oxley concludes that the free hydrogen atom is probably paramagnetic, but that the structure of the molecule must be such that by compensation of electronic rotations it is as a whole diamagnetic.   A

[28] P. D. Foote and F. L. Mohler, *J. Washington Acad. Sci.*, 1920, **10**, 435 ; *A.*, ii, 666.

[29] J. R. Ashworth, *Nature*, 1920, **105**, 516.   [30] *Ibid.*, 581.

diagrammatic representation of such a model was already given by Oxley.[31]

A further criticism of Bohr's theory of the hydrogen molecule is that it leads to a value for the heat of dissociation of the gas into neutral atoms which is too low, namely, 60,000 cal. per gram-molecule, the best observed value being 85,000 cal. The mechanism of this dissociation has been considered in some detail by M. Planck.[32] This quantity at sufficiently low temperatures is necessarily equal to the difference between the energy of the molecule and that of the two atoms Planck discusses three different modes of dissociation. On the first it is assumed that the electrons in atoms and in the molecules describe circular orbits with single quanta; on this basis, which is Bohr's original basis, the heat of dissociation is found to be 62,100 cal. On the second assumption, that in all the atoms and molecules those electronic orbits which possess less than one quantum are correspondingly probable, the heat of dissociation on the basis of the classical mechanics is infinite; on the theory of relativity it becomes 70,000 cal., a quantity which is much too great. The third assumption is that in addition to circular orbits the electrons perform pendulum movements; this leads to the much better value, 140,000 cal. Planck concludes that the assumption of circular orbits is not justified. Sommerfeld somewhat earlier had considered elliptical orbits, and had applied the principal of relativity to these in order to explain the fine line spectrum.

Attention has already been drawn to a further discrepancy between Bohr's theory and experiment, namely, the existence of positively charged hydrogen molecules as indicated by the work of Franck, Knipping, and Krüger. It has also been shown by Born (compare section on the energetics of the crystal lattice) that Bohr's theory is inapplicable to crystals.

Finally, a brief reference may be made to the work of L. Schames.[33] It is known that the moment of inertia of a molecule can be calculated from the chemical constant of the substance. Assuming the molecule to be a di-pole, it is possible to obtain the distance between the two charges from the moment of inertia, and from this, in turn, to calculate the electric moment by applying the quantum theory. Using the ring electron structure and carrying out these calculations for the case of water-vapour and carbon dioxide, Schames has obtained values for the electric moment which are much greater than those obtained by Jona on the basis of Debye's theory from the temperature-coefficient of the dielectric

[31] *Nature*, 1920, **105**, 327.

[32] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, 914 ; *A.*, ii, 423.

[33] *Physikal. Zeitsch.*, 1920, **21**, 156 ; *A.*, ii, 301.

capacity of the gas. The discrepancy suggests that the electrons are not arranged in a ring round the nucleus, but in some spatial arrangement, such as that given by the G. N. Lewis cubical atom model.

We now turn to the problem of the structure of the helium atom. On the theory of Bohr the helium atom is regarded as consisting of a nucleus carrying two positive charges with two electrons rotating in the same direction and in the same orbit around the nucleus. On this basis Bohr calculated the ionisation potential of helium to be 28·8 volts. The value actually found [34] is 25·0 volts in very pure helium, a result in good agreement with earlier measurements,[35] namely, 25·4 ± 0·25 volts. Whilst Bohr's theory, as already pointed out, appears to be exact for the simple case of an atom having one electron, that is, for the hydrogen atom and the positively charged helium atom, the discrepancy between the observed and calculated values of the ionisation potential of the neutral helium atom is sufficiently great to cast serious doubt upon the correctness of the model suggested by Bohr for this case and for all other cases involving more than one electron.

In connexion with helium, I. Langmuir [36] has shown recently that the experimental value may be accounted for by attributing to the electrons a type of motion first suggested by Landé in connexion with crystals—already considered in a previous section—in which the electrons do not complete a circular or elliptic orbit, but at a certain stage are made to retrace their path, owing to the repulsion of a neighbouring electron. The helium atom, as envisaged by Langmuir, consists of the nucleus and the two electrons lying in the same plane, the electrons being placed symmetrically with respect to the nucleus. The electrons move with equal velocities in this plane, one in a clockwise the other in an anti-clockwise direction. If there were no forces of repulsion between the two electrons, and if suitable velocities were chosen, the electrons would move in a single circular orbit about the nucleus, but in opposite directions. That is, they would pass through one another twice in each completed rotation. Owing to their mutual repulsion, however, as they approach one another, their velocity may be reduced to zero, and with suitable choice of velocity they may be made to retrace their path when only a part of the orbit has been traversed. In fact, they never cross a line drawn through the nucleus at right angles to the line joining the nucleus and electrons when the latter

[34] F. Horton and (Miss) D. Bailey, *Phil. Mag.*, 1920, [vi], **40**, 440 ; *A.*, ii, 660.

[35] J. Franck and P. Knipping, *Physikal. Zeitsch.*, 1919, **20**, 481 ; *A.*, ii, 72.

[36] *Science*, 1920, **51**, 605 ; *A.*, ii, 656.

are farthest apart. Langmuir has calculated that the path of each electron is very nearly an arc of an eccentric circle extending 77° 58′ each way from the mid-point of swing, as measured from the nucleus. The movement of each electron is analogous to the movement of a pendulum bob in which the string is somewhat lengthened as the bob swings towards its position of maximum potential energy. Applying the quantum theory, Langmuir finds that the radius vector for the electron at its mid-point is 0.2534×10^{-8} cm., which is roughly four-fifths of the radius of the completed orbit in Bohr's model. Even at the end of the swing the calculated radius (0.2882×10^{-8} cm.) is slightly less than that calculated by Bohr. The number of complete " oscillations " per second is 1.22 times the number of " revolutions " of the Bohr electrons. Finally, the ionisation potential calculated on the new type of motion and structure is 25.59 volts, which agrees reasonably well with the observed value. Not only is the ionisation potential accounted for in a much more satisfactory manner than it is on the Bohr model, but, by restricting the movement of the electrons to certain portions of the sphere surrounding the nucleus, as is done in the above model, we are obviously approximating to the conditions represented in the well-known octet theory of atomic structure, which in the hands of Langmuir has been shown to be the most satisfactory one from the chemical point of view.

The Mobility of Electrolytic Ions.

Attempts [37] have been made in recent years to account for the observed velocity of ions in a field of electric force by applying Stokes's well-known expression. According to this expression, the velocity should vary inversely as the radius of the ion. Whilst this conclusion is borne out more or less exactly by a considerable number of large and heavy ions, it is not borne out in the case of simple ions, especially those of the alkali metals. Thus the atomic volumes of the alkali metals increase from lithium to cæsium, and it can scarcely be doubted that the corresponding ions follow the same sequence. That is, the lithium ion should travel most rapidly, the cæsium least rapidly; this, however, is the reverse of what is found.

The difficulty has been explained on the familiar assumption of hydration, this term being employed to denote one or more definite stoicheiometric compounds of ion and water molecules. The

[37] R. Lorenz, *Zeitsch. anorg. Chem.*, 1919, **105**, 175 ; *A.*, 1919, ii, 212 ; R. Lorenz and I. Posen, *ibid.*, 1916, **94**, 265 ; *A.*, 1916, ii, 312 ; R. Lorenz, *Zeitsch. Elektrochem.*, 1920, **26**, 424 ; *A.*, ii, 729.

smaller the actual magnitude of the ion, the more intense is the electric field at its surface, and consequently the greater the tendency to attach water molecules. The latter process has been subjected to a fairly rigorous treatment by Born,[38] commencing with the idea that definite hydrates are not necessarily formed, but that, instead, a certain degree of condensation or compression of the water molecules occurs in the immediate neighbourhood of each ion, a water molecule being regarded as an electric di-pole [39] of known moment. A number of the water molecules, in virtue of their polarity, orientate themselves in a certain way with respect to the ion. When the latter is set in motion, the water molecules are dragged along with it, and so slow down the speed of the ion, each di-pole suffering at the same time a certain amount of torsion. These effects have been allowed for by Born in making use of Stokes's expression in its usual form, in which, however, an " apparent radius " term, r', is substituted for the actual radius, r. The relation between r and r' is given by the expression

$$r' = r\left(1 + \tfrac{1}{3}\left(\frac{r_0}{r}\right)^4\right),$$

where r_0 is a constant, called the characteristic radius, and is defined by

$$r_0 = \sqrt{\frac{anFM}{RT}},$$

in which F is the faraday, M the moment of the di-polar water molecule, R the gas constant, T the absolute temperature, n the valency of the ion, and a a quantity, the maximum value of which is unity, the minimum value being $1/\epsilon$, where ϵ is the dielectric capacity of the medium. The expression for r' (that is, the value which must be inserted in Stokes's expression in order to account for the observed velocity) becomes identical with the actual radius r for large ions. As we pass to a consideration of smaller ions, the value of r' falls to a minimum, given by $\tfrac{4}{3}r_0$, and then rises rapidly as r itself further falls, so that for very small ions the value of r' is decidedly greater than r.

A preliminary test of the validity of the expression for r' consists in showing that r_0 has the proper atomic dimensions. Inserting the usual values for n, F, R, T, and the value $M = 1.87 \times 10^{-18}$ e.s.u., as determined by M. Jona,[40] it is found that $r_0 = 1.47\sqrt{a}$. Since a varies between 1 and 1/81 for water, the value of r_0 lies

[38] Zeitsch. Elektrochem., 1920, 26, 401.
[39] Compare P. Debye, Physikal. Zeitsch., 1912, 13, 97 ; Ber. Deut. physikal. Ges., 1913, 15, 777.
[40] Physikal. Zeitsch., 1919, 20, 14 ; A., 1919, ii, 130.

between 10^{-7} and 10^{-8} cm.; that is, it is of the right order of magnitude.

The equation connecting r' and r can be applied quantitatively to the case of ions by assuming that the cæsium ion corresponds more or less exactly with the minimum value of the apparent radius, that is, $r'_{c_s} = \frac{1}{3} r_0$. The apparent radius for this ion is found experimentally to be $1 \cdot 11 \times 10^{-8}$ cm. Hence

$$r_0 = 0 \cdot 833 \times 10^{-8} \text{ cm.}$$

Employing this value, Born finds the following values of r and r' for a number of univalent ions:

Ion	Cs.	Rb.	K.	Na.	Li.	I.	Br.	Cl.
Apparent radius ($r' \times 10^8$)	1·11	1·12	1·17	1·74	2·26	1·13	1·12	1·15
True radius ($r \times 10^8$) ...	0·83	0·77	0·69	0·51	0·45	0·95	$\begin{Bmatrix} 0{\cdot}77 \\ 0{\cdot}92 \end{Bmatrix}$	0·73

The true radius is that calculated from the apparent radius by means of the equation first mentioned. The conclusion to be drawn is that in the case of the alkali ions, although the apparent radius increases as we pass from cæsium to lithium, this is not incompatible with the fact that the true radius diminishes. The discrepancy referred to at the beginning of this section is thus explained. It may be pointed out, however, that Born's theory, although satisfactory, cannot be regarded as numerically exact, owing to the doubt which exists in connexion with the value of a. Numerical values can only be obtained at the present time by making an assumption, necessarily somewhat in error, in connexion with the magnitude of the apparent radius of the cæsium ion.

Electrical Conductivity of Solid and Fused Salts.

In the Report for 1918 reference was made to the work of J. C. Ghosh on the anomaly of strong electrolytes, in which Milner's concept of complete ionisation at all dilutions was employed to account for the observed conductivity. The lattice theory of crystalline salts, reviewed in the first section of the present Report, involves, obviously, a structure analogous to that of complete ionisation. Ghosh [41] has applied his former method of treatment to the case of solid salts, pointing out that although ionisation is complete, the ions are not free to move until very high temperatures are attained. The number of free ions in the case of a uni-univalent salt is then given by

$$2n = 2Ne^{-W/2RT} \quad \ldots \quad \ldots \quad (1)$$

where N is the Avogadro constant and W is the work which must

[41] *T.*, 1920, **117**, 823.

be done at temperature T by the ions of 1 gram-molecule to over-come the elastic forces to which they are ordinarily subjected. It follows that the specific conductivity, μ, of a solid salt is expressed by the relation

$$\mu = \frac{U}{v} 2Ne^{-W/2RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the molecular volume of the salt and U the average mobility of the ions at the temperature T.

Ghosh considers that the variation of W with temperature may be obtained by an application of Nernst's heat theorem, the system being a condensed one, thus:

$$W = W_0 + \beta T^2.$$

The magnitude of W depends on the purely local forces at a point inside the solid, and may be regarded as running parallel with the elastic rigidity. Since the latter diminishes as the tempera-ture rises, W will diminish, and consequently β is a negative quantity. At the melting point, T_m, where the purely local part of the forces is negligible, Ghosh assumes

$$W = W_0 + \beta T_m{}^2 = 0.$$

β can thus be expressed in terms of W_0, so that, finally, we have

$$W = W_0\left(1 - \frac{T^2}{T_m{}^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The variation of the mobility, U, of an ion in a solid with rise in temperature is accounted for in a way analogous to the former electron theory of metallic conductors. This leads, finally, to the expression

$$U = \text{constant}/\sqrt{T} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

On combining (2), (3), and (4), we obtain

$$\frac{W_0(T_2 - T_1)}{2R}\left\{\frac{1}{T_1 T_2} - \frac{1}{T_m{}^2}\right\} = \log_e \frac{\mu_2 \sqrt{T_2}}{\mu_1 \sqrt{T_1}} \quad . \quad . \quad . \quad (5)$$

This expression contains only one unknown constant, W_0, which can be easily obtained from any two observed values of μ. On comparing the observed specific conductivities of solid salts with the values calculated by means of equation (5), satisfactory agree-ment is obtained. By way of illustration, the results obtained in the case of sodium chloride are quoted in the following table, the final column of which contains the activity-coefficient, a,[42] calcu-lated from equation (1), namely,

$$\frac{W}{2RT} = \log_e \frac{2N}{2n} = \log_e \frac{1}{a}.$$

[42] Compare *Ann. Reports*, 1917, **14**, 11.

Sodium Chloride.

$W_0 = 51 \cdot 2$ kilo.-cal. $T_m = 1083$ abs.

T abs.	μ calcd. $\times 10^6$.	μ observed $\times 10^6$.	a.
903	—	12·6	0·0127
923	21·2	21·2	0·0216
943	35·4	35·0	0·0363
983	91·0	95·0	0·0988
1023	240·0	240·0	0·2551
1073	729·0	729·0	0·8034

It may perhaps be pointed out that the values obtained by Ghosh for W_0 are very similar to the latent heat of sublimation at absolute zero calculated by Haber and Reis (compare first section of this Report). One would rather have expected W_0 to be analogous to a latent heat of fusion, the W term by definition representing a free energy change, the latent heat representing an internal energy term.

It follows from equation (3) above that at the melting point all the ions are free to move past one another, since W is zero at this temperature, and consequently the activity-coefficient as defined above becomes unity for fused salts [compare equation (1)]. Hence the specific conductivity of fused salts does not vary with the temperature in a logarithmic manner. This is to be expected, as all the ions present contribute to the conductivity. The latter is thus found, in agreement with experiment, to vary linearly with the temperature, such variation being due entirely to a change in the mobility of the ions.

W. C. McC. LEWIS.

INORGANIC CHEMISTRY.

MANY papers have been published on orthodox inorganic chemistry during the last year, and several of these awaken more than a passing interest. There have appeared, however, four papers by Aston, Rutherford, Harkins, and Wendt and Landauer, which outshine all others in importance, for without question they bid fair to revolutionise the fundamental conceptions of chemistry. Whilst by some the signs of the impending change have been recognised, the majority of chemists must now awaken to the fact that a new philosophy is being born. The brilliant discoveries of Soddy and Fajans of the existence of isotopes mark the first real step after the discovery of the production of helium in the radioactive disintegration of atoms. About the same time Thomson, Collie, Patterson, and Masson stated that helium and neon are produced in hydrogen-filled vacuum tubes under the influence of a powerful electric discharge. Very soon afterwards appeared the Harkins theory that all elementary atoms are built up either of helium atoms or of atoms of helium and hydrogen. Last year the next step was gained when Rutherford succeeded in disrupting the atom of nitrogen.

It may now be said that the whole story is practically complete, and a wonderful story does it prove to be. Perhaps the most startling of all the new knowledge gained is that on the oxygen standard all atomic weights, with the exception of hydrogen, are exact whole numbers, and that the fractional values we have accepted as the result of highly accurate work are merely fortuitous statistical averages due to a mixture of two or more isotopes. Whilst this has been proved by experiment, it also is a necessary corollary of the theories of atomic structure. In the annual Report for 1917 reference was made to Harkins' theory that all elementary atoms are built up of helium atoms or helium and hydrogen atoms This theory has now been published in its complete form, and it carries conviction in its train. An essential feature is that the hydrogen isotope H_3 plays an integral part in atomic structure, that it has a definite power of existence, and that very probably it is

identical with the nebular material called nebulium. First detected by Thomson, then more fully confirmed by Aston, H_3 has now been prepared from hydrogen.

Then, again, Rutherford has shown that by the disruption of the atoms of oxygen and nitrogen an element of mass 3 is produced, which, however, is an isotope of helium. Rutherford considers that the atom of mass 3 which enters into the nuclear structure of atoms is this helium isotope and not H_3 as Harkins assumes.

Whichever view may prove to be correct, there can now be little doubt that all elementary atoms are built up from helium or from helium and atoms of mass 3, and, moreover, it is accepted by the new school that helium itself is built up from four atoms of hydrogen. The added importance of Collie's work on the formation of helium and neon in hydrogen-filled vacuum tubes is manifest, for it has now become an obvious result from the new theories.

Another most interesting aspect of this new knowledge is that the synthetic process whereby our elements are known to be produced during the life history of the stars from the original nebulium by way of hydrogen and helium can now be understood.

It is difficult to write of these discoveries and theories in a calm and measured fashion. They are so great in their achievement, so stupendous in their meaning, and so subversive in their effect that some enthusiasm may perhaps be allowed to him who records them. Strange it is that after all these years the old hypothesis of Prout should rise triumphant, for, in a word, it is this that has occurred. In the Report for 1914, when the discovery of isotopes and Collie's work had been announced, the writer ventured to write the following words: "As did his forefathers of pre-Avogadro days, so also does he (the chemist of to-day) now await that great generalisation which shall co-ordinate and link up all the threads to found a new philosophy. Radioactivity, enhanced line spectra, the intra-stellar elements, active nitrogen and oxygen, atomic disintegration, atomic-weight variation, all will be unified and embodied in the new philosophy of the twentieth century. Then will a new chemistry in its greater meaning emerge as a phœnix from the glowing parental fires of the many chemistries of to-day."

Little apology is needed for making this quotation, since the prophecy seems to be almost complete in its fulfilment.

Atomic Theory.

In the Reports for 1913 and 1914 reference was made to the work of Thomson, of Collie and Patterson, and of Masson on the production of helium and neon from hydrogen at low pressures under

the influence of the electric discharge. Negative results were recorded by Strutt and by Merton, but Collie, using Merton's own apparatus, obtained definite evidence of the formation of both these gases. Some further experiments have been carried out during this year, and once more negative results have been obtained.[1] In view of the fact that Collie himself more than once obtained negative results when using different induction coils, the writer suggested that the explanation of the divergence of the results obtained by different observers is to be found in the fact that a particular type of discharge is necessary. Piutti and Cardoso, whilst admitting that our rudimentary knowledge does not permit us to discuss this explanation, point out that their results strengthen the probability against it. They say that as in the somewhat analogous case of active nitrogen, where considerable divergence of opinion existed, it would be advisable that joint work be carried out systematically in order definitely to settle this important question.

There is little doubt that the trend of recent ideas will create less antagonism to the formation of helium and neon in vacuum tubes than was the case six years ago. The work of Rutherford on the disintegration of nitrogen and oxygen atoms has undermined the old confidence in the immutability of the atom. On the other hand, all other experimental work has been in the direction of the disruption of atomic nuclei, whilst Collie's work means a synthesis of atomic nuclei heavier than the parent hydrogen.

There can be no question that one of the most complete theories advanced as regards the structure of atomic nuclei is that by Harkins.[2] His earlier papers were reviewed in the Report for 1917. According to this theory, the elements are of two kinds, namely, those of even atomic number, the atomic nuclei of which are composed of helium nuclei alone, or helium nuclei together with cementing electrons, and those of odd atomic number, the nuclei of which are composed of helium and hydrogen nuclei together with cementing electrons. Further, the helium nucleus consists of four hydrogen nuclei, together with two cementing electrons, the loss of mass being due to the packing effect. The helium nucleus is the most stable configuration of all, whilst next in order of stability comes the group of atoms or even atomic number. An interesting fact arises in connexion with the number of hydrogen nuclei which are associated with the helium nuclei in the second class of elements. In the case of the lighter elements with odd atomic number this number is always three save in the exceptional case of nitrogen,

[1] A. Piutti and E. Cardoso, *J. Chim. phys.*, 1920, **18**, 81 ; *A.*, ii, 311.

[2] W. D. Harkins, *Physical Rev.*, 1920, **15**, 73 ; *A.*, ii, 479.

where it is two. The extremely frequent occurrence of this group of three hydrogen nuclei suggests that it probably occurs alone as a unit with a nuclear charge equal to 1 and atomic weight of 3, and therefore structurally it will be an isotope of hydrogen. If the hypothetic nebulium exists at all it is probably this form of hydrogen, and it is interesting that from a study of the Döppler effect the atomic weight of this element has been found to be about 3.[3]

Now there is one point in connexion with the Harkins theory which requires consideration. If, for example, the elements with even atomic numbers are formed from helium nuclei, why is it that they are not more unstable in view of the fact that the helium atom is the most stable form? It would seem necessary to conclude that the elements are metastable, and that they are able to exist owing to their possessing an external force field. If this is broken by the supply of energy, then the atomic nucleus will become unstable. If this principle of external fields is accepted, then it only becomes a question of supplying the right amount of energy to the hydrogen atom for the association to become possible of three or four nuclei to form H_3 or helium. On the Harkins theory, therefore, there is no reason against the production of H_3 and helium in vacuum tubes from hydrogen if the discharge employed produces the suitable type of energy. Indeed, such a phenomenon is rather to be expected than denied in view of the stability of the helium nucleus. The writer is therefore all the more encouraged to insist on the correctness of his suggestion made in 1914 that the contradictory results obtained by Thomson, Collie, Patterson, and Masson on the one hand, and by Strutt, Piutti and Cardoso on the other, are due to the absence of sufficient energy of the right kind in the latter and negative experiments. There are two alternative possibilities as to the nature of the energy required to break open the fields of the hydrogen atom. It may either be radiant energy of short wave-length or it may be energy given by rapidly moving particles. The production of either of these in a given vacuum tube varies remarkably with the conditions. The importance of this work has undoubtedly increased, and it is a matter of some moment that the question as to the production of helium from hydrogen be decided.

Reference may here be made to a branch of investigation which, although not chemical, must possess great interest for the inorganic chemist, namely, stellar development. According to the modern views of astro-physicists there is little doubt that in the stars a development process is taking place whereby the chemical elements are being synthesised from hydrogen and helium as parents. Now

[3] C. Fabry and H. Buisson, *Astrophys. J.*, 1914, **40**, 256.

it would seem fairly certain from a study of the spectra and rotational velocities of certain nebulæ, particularly the one in Orion, that the original material from which the synthetic process starts is nebulium, which as the first stage in the process forms hydrogen and helium. When it was discovered that the probable atomic weight of this gas is 3, it appeared somewhat incomprehensible that a synthetic process should give both hydrogen and helium. In all probability, on the basis of Harkins' theory that nebulium is H_3 the first stage is the formation of hydrogen, which then associates to give helium, which in its turn associates to give elements of even atomic numbers. If this is so, by far the greatest amount of condensation will take place in the direction of the elements of even atomic numbers. The great predominance of elements of this class has been pointed out by Harkins, who offers two explanations of the relative scarcity of the elements with odd atomic numbers which consist of helium and H_3 atoms. First, their scarcity may be due to their relative instability, and secondly, there may have been present during the synthetic process relatively little H_3. The first alternative is unsatisfactory, for at present there seems little, if any, direct evidence that the elements of odd atomic numbers are less stable than their fellows. The second alternative fits in very well with the present suggestion, since, if the first stage is the production of hydrogen from H_3, and the second stage is the formation of helium from the hydrogen, it is probable that in any later association there will be present only small amounts of H_3. The Harkins theory would therefore fill an undoubted gap in the theories of stellar development.

An important paper has appeared during the year on the mass spectra, or positive ray spectra, of the elements by Aston, who describes his apparatus in detail and the most recent results he has obtained.[4] The principle of the method consists in producing the positive rays with a given element and passing them through slits. The rays also pass through an electric field and a magnetic field, and then impinge upon a photographic plate. A focussed spectrum is obtained in which the lines depend solely on the ratio of mass to charge. By varying the strengths of the two fields, any desired line may be brought on to the centre of the plate. All the measurements of the positions of the various lines are relative, and so one element must be taken as standard, and for this purpose oxygen was selected. The molecule of oxygen carries one charge, whilst the atoms carry one or two charges, with the result that with this gas three lines are obtained. The three lines are obtained at the scale readings 32, 16, and 8 respectively. Direct comparison

[4] F. W. Aston, *Phil. Mag.*, 1920, [vi], **39**, 611 ; *A.*, ii, 344.

of the carbon, carbon monoxide, and carbon dioxide lines with these standards gave C++ (6), C (12), CO (28), and CO_2 (44). Clearly, therefore, the whole number relation and the additive law hold within the limit of accuracy, which is one part in a thousand.

The following results have been obtained with eleven elements. Neon, with an atomic weight of 20·2, gives two well-defined lines which correspond with masses 20 and 22 respectively. This gas, therefore, consists of two isotopes, with possibly a third, of mass 21, since there was observed a very faint line in this position.

Chlorine shows four very definite lines, corresponding with masses 35, 36, 37, and 38, with no indication whatever of a line corresponding with its atomic weight of 35·46. There is no escape, therefore, from the conclusion that chlorine is a mixture of isotopes, and that two of these have masses 35 and 37. Whilst the lines 36 and 38 may be due to two more isotopes, it is more probable that they are given by the hydrogen compounds of the two isotopes with masses 35 and 37. Strong lines were also observed at 63 and 65, due, no doubt, to the carbonyl compounds of the two isotopes. Again, if ordinary chlorine of average atomic mass 35·46 is a mixture of two isotopes 35 and 37, it is evident that the line of 35 should be stronger than the line of 37, and this was actually found to be the case. A faint line was distinguishable at 39, which possibly is due to a third isotope.

Argon shows three strong lines at 40, 20, and 13·33, which clearly correspond with particles of mass 40, carrying 1, 2, and 3 charges respectively. A faint companion was seen at 36, which is doubtless due to an isotope present in small amounts. The presence of about 3 per cent. would account for the fractional atomic weight determined from the density.

Nitrogen gives a line which cannot be distinguished from that of carbon monoxide, and a second line at 7, due to a doubly charged particle. Evidently, therefore, no isotope is present and nitrogen is a pure element.

The measurements with hydrogen were more troublesome, owing to the fact that the position of the lines is so far removed from the reference standards. The difficulty was surmounted by comparing helium with the doubly charged atoms of oxygen and carbon (8 and 6), Thomson's H_3 with carbon and helium, and hydrogen with helium. The results show definitely that both hydrogen and helium are pure elements, and that the mass of the helium atom is 4. The mean value for the mass of H_3 is 3·026, and that for the mass of the hydrogen molecule is 2·015. The atomic mass of hydrogen, therefore, is clearly 1·008, and the nature of the H_3 molecule is settled beyond question.

Krypton was found to exhibit perfectly definite evidence of being a mixture of five isotopes of masses 80, 82, 83, 83, and 86, with a probable sixth of mass 78. Measurements of these lines were made with singly, doubly, and trebly charged particles. There would seem, also, to be five isotopes present in xenon, with masses 128, 130, 131, 133, and 135, but as only a minute quantity of this gas was available these results are only provisional.

Mercury was also found to be complex, for the lines observed indicate the presence of a strong component 202, and a weak one 204. There is also a strong band from 197 to 200, indicating three or four more components, but up to the present this band has not been resolved.

Perhaps the most important generalisation that can be made from this work is the quite remarkable fact that with the exception of H_2 and H_3 all masses, atomic and molecular, elementary and compound, so far measured are whole numbers within the accuracy of experiment. The number and variety of substances studied make the probability of this being true for all elements extremely great. It certainly allows of hypotheses being put forward of atomic structure far simpler than those which attempted to explain fractional atomic weights, since these now appear to be merely fortuitous statistical effects, due to the relative quantities of the isotopic constituents. Thus it may now be supposed that an elementary atom of mass M may be changed to one of mass $M+1$ by the addition of a positive particle (H) and an electron. If both enter the nucleus an isotope results, for the nuclear charge is unaltered. If the positive particle alone enters the nucleus, an element of the next higher atomic number is formed. When both forms of addition give a stable configuration the new elements will be isobares.

Apart from the intrinsic value of Aston's work, its importance becomes very pronounced when considered along with theories of the nuclear structure of atoms. These lead undoubtedly to integral values of atomic weights, and Harkins explains the divergence from whole numbers by the existence of isotopes. These isotopes have now been shown by Aston to exist, and it is of interest to note that Harkins has obtained evidence of the separation of chlorine into two isotopes by diffusion experiments with hydrogen chloride.[5]

On the other hand, Rutherford[6] has published further experimental data which, to a certain extent, do not fit in with Harkins' theory. When the swiftly moving particles from radium-C pass

[5] W. D. Harkins, *Science*, 1920, **51**, 289.

[6] (Sir) Ernest Rutherford, *Proc. Roy. Soc.*, 1920, [A], **97**, 374 ; *A.*, ii, 541.

through nitrogen, some of the atomic nuclei of this gas are disrupted, and, as is now well known, hydrogen atoms are produced. Hydrogen atoms are not produced in oxygen under the same conditions. It is found, however, that both oxygen and nitrogen give slower moving particles of mass 3 with charge 2. The nitrogen nucleus, therefore, can be disintegrated in two ways, one by the expulsion of the hydrogen atom, and the other by the expulsion of an atom of mass 3 carrying two charges. Since these atoms of mass 3 are five to ten times as numerous as the hydrogen atoms, it appears that these two forms of disintegration are independent and not simultaneous. It would follow also that the new atom when it has gained two electrons should have physical and chemical properties very nearly identical with those of helium, but with mass 3 instead of 4. The spectra of helium and this isotope should be nearly the same, but, on account of the marked difference in the relative masses of the nuclei, the displacement of the lines should be much greater than in the case of the isotopes of heavy elements like lead. It is very improbable that this isotope is connected with nebulium.

In dealing with the nuclear constitution of the lighter elements, Rutherford naturally assumes that the new helium isotope forms an integral part of these nuclei. Thus he suggests that the carbon atom consists of four atoms of the helium isotope and that the nitrogen atom consists of four of these isotopes and two hydrogen atoms, whilst the oxygen atom is built up of four helium isotopes and one helium atom. It will be seen at once that there is an essential difference between this view and that put forward by Harkins, who considers that the carbon and oxygen atoms consist of three and four atoms, respectively, of ordinary helium.

Now there seems no doubt that the helium isotope discovered by Rutherford is a different entity from H_3, which forms an integral part of Harkins' theory, was first discovered by Thomson, now confirmed by Aston, and has recently been directly prepared by the activation of hydrogen.[7] Aston has definitely shown that H_3 carries one charge, and this fact, considered along with its formation from hydrogen, shows that it is an isotope of hydrogen. There thus exist two elements of mass 3, one an isotope of hydrogen and the other an isotope of helium. It is not possible yet to say definitely whether either alone or both together take part in atomic nuclear synthesis.

In this connexion, the writer would draw attention to the very remarkable permanent contraction suffered by hydrogen when it

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[7] G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1920, **42**, 920; *A.*, ii, 425.

has been activated and lost its activity. This point is detailed in the section of this Report dealing with the first group of elements. Wendt and Landauer assume, of course, that H_3, on keeping, regenerates ordinary hydrogen, but is it absolutely certain that this is the case ? Collie's results on the formation of helium in vacuum tubes containing hydrogen, his collateral results on the permanent diminution in the volume of hydrogen in vacuum tubes, considered in connexion with the theories of atomic nuclear structure, lead inevitably to the conclusion that H_3, on keeping, gives little H_2, but mainly helium. Although this suggestion may sound very improbable to many, it is, in reality, far more probable than an ordinary chemical explanation, since it is scarcely possible to conceive that H_3 in the presence of nitrogen would not form ammonia, but prefer to react with the glass of the reaction vessel. This suggestion has been privately communicated to Dr. Wendt.

Atomic Weights.

The Report of the International Committee recommends only one change, namely, that the atomic weight of scandium should be raised from 44·1 to 45·1. The work of Hönigschmid, on which the new value is based, was referred to in last year's Report.

Three series of determinations have been made of the atomic weight of tin. Two of these involved the analysis of tin tetrabromide by silver,[8, 9] and the third depended on the direct electrolytic estimation of tin in the tetrabromide.[10] The values obtained were 118·700, 118·699, and 118·703, respectively, which agree very well with the accepted value.

The weight of a normal litre of methyl fluoride has been found to be 1·54542 grams as the mean of twenty-three determinations.[11] From this, the atomic weight of fluorine is deduced as 18·996, which is very close to the accepted value of 19.

Some determinations have been made of the atomic weight of samarium by the anhydrous chloride–silver ratio.[12] As the mean of eighteen determinations, the value of 150·43 was obtained.

In addition to the above, the following investigations may be reported. A determination has been made of the atomic weight of silicon by the analysis of silicon tetrachloride.[13] The mean of

[8] B. Brauner and H. Krepelka, *J. Amer. Chem. Soc.*, 1920, **42**, 917 ; *A.*, ii, 437.   [9] H. Krepelka, *ibid.*, 925 ; *A.*, ii, 437.

[10] G. P. Baxter and H. W. Starkweather, *ibid.*, 905 ; *A.*, ii, 436.

[11] E. Moles and T. Batuecas, *J. Chim. phys.*, 1919, **17**, 537 ; *A.*, i, 283.

[12] A. W. Owens, C. W. Balke, and H. C. Kremers, *J. Amer. Chem. Soc.*, 1920, **42**, 515 ; *A.*, ii, 316.

[13] G. P. Baxter, P. F. Weatherill, and E. O. Holmes, jun., *ibid.*, 1194 ; *A.*, ii, 487.

four experiments gave the value of 28·11, but as this is not accepted as final by the authors, this value must await confirmation.

By the analysis of bismuth chloride, a new value for the atomic weight of bismuth has been obtained.[14] The ratio $BiCl_3 : 3AgCl$ gave 209·024, and the ratio $BiCl_3 : Ag$ gave 209·027. The mean value 209·026 is one unit higher than the value at present accepted.

Colloids.

A few papers have appeared on the preparation and properties of inorganic colloids, and mention may be made of the following. A convenient method for the preparation of metallic sols [15] is to strike an arc between poles of the metal under alcohol, using capacity in the circuit. With a current of 1·5 amperes and a capacity of $12·8 \times 10^{-3}$ MF, colloidal solutions have been obtained of aluminium, antimony, bismuth, cadmium, copper, gold, lead, platinum, silver, and zinc. The colloidal metal is produced much more rapidly than by the earlier Svedberg method. The stability of the sols is fairly great, and although a certain amount always separates, the bulk of the metal remains in solution. Gold and platinum are exceptional, since their sols are very unstable.

Colloidal rhodium [16] has been prepared by the addition of a slightly alkaline solution of formaldehyde to a slightly alkaline solution of the double chloride, Na_3RhCl_6, the reduction being carried out at 40°. Under these conditions, a clear, colloidal solution of rhodium is obtained. This solution absorbs hydrogen to the extent of 2510—2960 times the volume of rhodium present. Similarly, the rhodium absorbs 346 times its volume of carbon monoxide at 12—14°, and 1820 times its volume at 60°. The colloidal solution, slightly alkaline, causes a very slight combination of nitrogen and hydrogen to give ammonia, the reaction being considerably enhanced if the solution is made just acid with very dilute tartaric acid in the presence of potassium tartrate.

Mention may also be made of some work on the preparation and stability of mercury sols.[17] The most concentrated solution is obtained by passing a rapid stream of mercury vapour into cold water, but in every case the sols are not very stable. Their stability is materially increased by the use of gum arabic as a protective colloid.[18]

[14] O. Hönigschmid and L. Birckenbach, *Zeitsch. Elektrochem*, 1920, **26**, 403 ; *A.*, ii, 549.

[15] G. Börjeson and T. Svedberg, *Kolloid Zeitsch.*, 1919, **25**, 154 ; *A.*, ii, 21.

[16] C. Zenghelis and B. C. Papaconstantinou, *Compt. rend.*, 1920, **170**, 1058 ; *A.*, ii, 380.   [17] I. Nordlund, *Kolloid Zeitsch.*, 1920, **26**, 121 ; *A.*, ii, 376.

[18] A. Gutbier and G. L. Weise, *ibid.*, 1919, **25**, 97 ; *A.*, ii, 36.

The Rare Gases.

Mention must be made of McLennan's work on the production of helium on the large scale from natural gases.[19] A large number of gases from natural sources in various countries was investigated, and the Bow Island gas supplied to the town of Calgary, in Alberta, was selected. This gas consists of methane 91·6, ethane 1·9, nitrogen 6·14, and helium 0·36 per cent., together with traces of carbon dioxide and water vapour. It is not possible to give details of the experimental plant employed, which followed the lines of the Claude oxygen-producing column. By its means, in two stages of working helium, was obtained of 87—90 per cent. purity. By the use of a second plant, this was further purified to 98—99 per cent. From the experience gained with these experimental plants, specifications have been drawn up for a commercial plant to deal with the whole of the Bow Island supply of gas. Six units are proposed, each dealing with about 62,000 cubic feet per hour, the average daily supply of gas being 9,500,000 cubic feet. The yearly output of helium of 97 per cent. purity would be about 10,500,000 cubic feet, and the working cost would be considerably less than £10 per 1000 cubic feet.

Group I.

A most interesting paper has been published on the formation [20] of triatomic hydrogen by various means from ordinary hydrogen. Hydrogen at atmospheric pressure, when submitted to the action of α-rays from radium emanation or passed through a silent discharge tube, is converted into an active form, and a similar result is obtained when the electric discharge from a large induction coil or transformer is passed through a vacuum tube, through which hydrogen is passed under a pressure of 2—8 cm. In each case, a small amount of an active form of hydrogen is produced, which is at once condensed on passing the hydrogen through a spiral tube cooled in liquid air. This active modification reacts with sulphur, arsenic, phosphorus, mercury, and nitrogen, and also reduces acid and neutral solutions of potassium permanganate. The amount of hydrogen that is converted into the active form in the experiments described has not exceeded 0·02 per cent.

Very careful experiments have proved that the enhanced reactivity is not due to the presence of ions, and also the substance

[19] J. C. McLennan, *T.*, 1920, **117**, 927.

[20] G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1920, **42**, 930 ; *A.*, ii, 425.

differs in its chemical and physical properties from atomic hydrogen prepared by Langmuir, which was referred to in the Reports for 1912 and 1915. The polyatomic nature of the substance is indicated by the contraction in volume of the hydrogen when it is formed, and, moreover, positive ray analysis has shown the undoubted existence of H_3 molecules when the electric discharge is passed through hydrogen at low pressures. There is little doubt that the substance is indeed H_3.

It is very unstable, and disappears very rapidly after it has been formed. This was shown by the increased reactivity that is observed when the flow of hydrogen through the silent discharge tube is increased. At atmospheric pressures it is found that the reactivity disappears within about one minute.

Perhaps the most interesting phenomenon in these experiments is the permanent contraction that takes place in the hydrogen. This was noticed by Usher,[21] who carried out experiments on the synthesis of ammonia by exposing a mixture of hydrogen and nitrogen to the action of α-rays from niton mixed with the gases. In one case, a contraction of 0·24 c.c. was observed, but only 0·006 c.c. of ammonia had been formed. Collie and Patterson[22] observed a similar disappearance of 3·6 c.c. out of 4·6 c.c. of hydrogen when the gas was sparked under reduced pressure with copper or aluminium electrodes. A possible explanation of this phenomenon is put forward in an earlier section of this Report, and it would, indeed, seem that this may prove to be even more interesting than the preparation of H_3, great as is the importance of this advance.

Investigation has shown that lithium behaves similarly to sodium and potassium in forming soluble silicates containing a large excess of the acid over the base.[23] Lithium metasilicate, Li_2SiO_3, has been prepared in an insoluble and a soluble modification, the former having the formula Li_2SiO_3,H_2O.

Brief reference may be made to some experiments on the action of alcohol on the sulphates of sodium.[24] Dry alcohol acts on dry sodium hydrogen sulphate to give the intermediate sulphate, $Na_2SO_4,NaHSO_4$, and free sulphuric acid, which dissolves in the alcohol. No action takes place with potassium hydrogen sulphate. In the presence of moisture, sodium hydrogen sulphate is first converted into the intermediate sulphate, and then, finally, into

[21] F. L. Usher, *T.*, 1910, **97**, 389.

[22] J. N. Collie and H. S. Patterson, *P.*, 1913, **29**, 22, 217.

[23] K. A. Vesterberg, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 30; *A.*, ii, 112.

[24] G. S. Butler and H. B. Dunnicliff, *T.*, 1920, **117**, 649.

ordinary sodium sulphate. When an alcoholic solution of sulphuric acid (20 per cent. or less) acts on sodium sulphate in the cold, the intermediate sulphate is formed. Nitre cake consists of $Na_2SO_4,NaHSO_4$ alone or mixed with either $NaHSO_4$ or Na_2SO_4, according as the acidity is equal to, greater than, or less than, 18 per cent. H_2SO_4.

A process has been patented for the preparation of metallic potassium by heating potassium hydroxide and sodium in exactly equivalent proportions at 670° in the absence of air.[25] Hydrogen is produced and the potassium is volatilised and may be condensed.

Some further and, it may be said, conclusive work has been carried out on the possible existence of an alkali metal of higher atomic weight than cæsium.[26] The alkalis were separated from 3500 grams of pollucite, which contains more than 30 per cent. of cæsium oxide, and the mixture was carefully tested for the presence of the next higher homologue to cæsium. There is no need to describe the experimental details, but no indication whatever was found of the presence of a new element.

Group II.

A study has been made of the equilibrium conditions which obtain between arsenic oxide, calcium oxide, and water at 35° for those mixtures in which the arsenic oxide is in excess.[27] Evidence was found of the existence of two orthoarsenates of calcium, namely, dicalcium orthoarsenate monohydrate, $CaHAsO_4,H_2O$, and monocalcium orthoarsenate, $CaH_4(AsO_4)_2$. The former is identical with the mineral haidingerite, and is stable in contact with a solution containing more than 27·5 per cent. of arsenic oxide, whilst the latter is stable with a lower percentage of arsenic oxide in the solution.

Mention may be made of the fact that chlorine has no action on calcium carbide, whilst liquid bromine slowly reacts to give hexabromoethane and calcium bromide.[28] The reaction is very slow, and 4·5 grams of the finely-powdered carbide treated with 45 grams of dry bromine for five weeks gave 22 grams of hexabromoethane, 8·8 grams of calcium bromide, and 0·2 gram of unchanged carbide.

Reference was made in the Report for last year to the fact that the decomposition of barium peroxide takes place at a much lower temperature in the presence of silica, a certain amount of barium

[25] F. C. Wickel and W. Loebel, *D.R.-P.* 307175 ; *A.*, ii, 32.
[26] L. M. Dennis and R. W. G. Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 985 *A.*, ii, 431. [27] C. N. Smith, *ibid.*, 259 ; *A.*, ii, 375.
[28] E. Barnes, *Chem. News*, 1919, **119**, 260 ; *A.*, ii, 33.

silicate being formed. The influence of a great number of other oxides has now been studied by examining the heating curves of the mixtures in molecular proportions.[29] Cuprous oxide reacts violently with barium peroxide to give cupric oxide, which decomposes barium peroxide catalytically, the optimum temperature being about 660°. Magnesium and calcium oxides start the decomposition of the peroxide at 250° and 310° respectively, whilst zinc oxide causes slow decomposition between 200° and 370° and forms barium zincate. Zirconium oxide, stannous oxide, and stannic oxide have no action, but the oxides of cadmium, lanthanum, and cerium act as pure catalysts. Aluminium oxide forms barium aluminate, and titanium oxide in molecular proportions gives a titanate, probably $BaTiO_3$. With twice the molecular proportions of barium peroxide a basic titanate is produced. Litharge and barium peroxide between 300° and 400° evolve no oxygen, but form a brown substance of unknown composition. Above 500° much oxygen is evolved, with the probable formation of Ba_2PbO_4. Vanadium pentoxide reacts vigorously with barium peroxide. When equimolecular proportions are used, the reaction begins at 215° and is ended at 530°, $Ba(VO_3)_2$ being formed. With $2BaO_2$ the metavanadate is first formed, but at 375° a second, very vigorous, reaction starts and the colour changes from brown to white, the product apparently being $Ba_2V_2O_7$. Tantalum pentoxide also reacts vigorously to give a tantalate. With arsenious oxide and three molecules of barium peroxide, arsenic oxide is first formed at 310° to 440°, and above 465° oxygen is evolved and barium arsenate is formed. With antimony oxide at 200° oxygen is evolved with almost explosive violence. Bismuth oxide starts a gradual evolution of oxygen at about 250°, and higher bismuth oxides, or compounds of these with barium peroxide, appear to be formed. With chromium oxide no oxygen is evolved, and barium chromate is produced. The oxides of molybdenum, tungsten, and uranium all cause evolution of oxygen and form molybdates, tungstates, and uranates respectively. The lower oxides of manganese are all oxidised and give barium manganate. Ferric oxide acts catalytically, and gives barium ferrate, whilst nickel and cobalt also act catalytically and are changed into higher oxides, which do not agree in their properties with the known peroxides of these metals.

It has been found that strontium sulphide is readily hydrolysed by water to give equimolecular proportions of the hydrosulphide and the hydroxide.[30] These two compounds do not form a mixed

[29] J. A. Hedvall and N. von Zweigbergk, *Zeitsch. anorg. Chem.*, 1919, **108**, 119 ; *A.*, ii, 35.

[30] K. Brückner, *Zeitsch. Elektrochem.*, 1920, **26**, 25 ; *A.*, ii, 251.

compound, and the hydroxide may be separated by crystallisation. When strontium sulphide is extracted with hot water and the clear filtrate cooled, pure strontium hydroxide, $Sr(OH)_2$, crystallises. The case is different with barium sulphide, as the hydroxide and hydrosulphide form an additive compound, $OH \cdot Ba \cdot SH, 5H_2O$.[31] Under no conditions can pure barium hydroxide be crystallised from the solution obtained by the action of water on barium sulphide.

From a study of the equilibrium between zinc oxide, phosphoric oxide, and water at 25° and 37°, the following phosphates of zinc have been found to exist: $Zn_3(PO_4)_2, 4H_2O$, $ZnHPO_4, 3H_2O$, $Zn(H_2PO_4)_2, 2H_2O$, whilst at 37° an additional salt, $ZnHPO_4, H_2O$, is obtained.[32] Similar investigations with sodium hydroxide solutions and zinc oxide have established the existence of $Na_2O, ZnO, 4H_2O$ as a stable compound.[33]

Group III.

An investigation has been made of the equilibrium conditions between aluminium nitrate, nitric acid, and water at 25°, and it was found that three hydrates of the salt have a stable existence.[34] The first, $Al(NO_3)_3, 18H_2O$, is most stable in contact with the solution containing 73 per cent. or less acid, the second, $Al(NO_3)_3, 16H_2O$, is stable with 73—81 per cent. acid, whilst the third, $Al(NO_3)_3, 12H_2O$, is stable in the presence of more than 81 per cent. of nitric acid.

Some physical measurements have been made of the solutions obtained by dissolving aluminium in aqueous solutions of sodium hydroxide and of ammonium hydroxide.[35] Whilst the physical aspect of this work does not fall within the purview of this Report, the results have some value for inorganic chemists. It is shown that aluminium hydroxide neutralises the alkalis as a monobasic acid, and that the aluminates are salts of the acid $HAl(OH)_4$, that is, $Al(OH)_3, H_2O$. Ammonium aluminate, $NH_4Al(OH)_4$, is quite stable in solution.

Some further work may be reported on scandium fluoride and the scandifluorides.[36] The best method for the preparation of the

[31] K. Brückner, *Zeitsch. Elektrochem.*, 1920, **26**, 1 ; *A.*, ii, 252.

[32] N. E. Eberly, C. V. Gross, and W. S. Crowell, *J. Amer. Chem. Soc.*, 1920, **42**, 1433 ; *A.*, ii, 545.

[33] F. Goudriaan, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179 *A.*, ii, 113.

[34] K. Inamura, *J. Tokyo Chem. Soc.*, 1920, **41**, 1 ; *A.*, ii, 625.

[35] J. Heyrovský, *T.*, 1920, **117**, 1013.

[36] J. Stěrba-Böhm, *Bull. Soc. chim.*, 1920, [iv], **27**, 185 ; *A.*, ii, 315.

pure fluoride is by the action of hydrofluoric acid on scandium oxide, the product being finally heated at 150—180° in order to remove the excess of hydrofluoric acid. Whilst the free scandifluoric acid does not exist, two new ammonium scandifluorides have been prepared. The salt, $(NH_4)_3ScF_6$,[37] is hydrolysed in the presence of ammonium fluoride to give in quadratic crystals the salt, $(NH_4)_2ScF_5$. In warm or cold water alone the salt, $(NH_4)ScF_4$, is always obtained as a microcrystalline powder. By the dissolution of scandium fluoride in a concentrated solution of silver fluoride a scandifluoride of silver is formed.

It is known that lead nitrate and nitrite interact in solution to give well-defined compounds containing both salts. Similarly, thallium nitrite and lead nitrate react to give basic compounds of both salts.[38] In the case of potassium nitrite and thallium nitrate no such double salts are obtained, but thallium nitrate—nitrites are formed which are stable and can be crystallised unchanged. With two molecules of potassium nitrite and one molecule of thallium nitrate the compound formed has the formula $Tl_3N_3O_8$. With different proportions other salts are obtained, in which the ratio between nitrate and nitrite is not a simple one.

Group IV.

Since last year's Report was written Sir Charles Parsons has published a complete account of his experiments on the artificial production of diamond.[39] It is shown beyond any doubt that high pressure alone is not sufficient to cause the conversion of graphite into diamond, and it is also shown that iron must be present. Experiments in which a mixture of acetylene and oxygen is highly compressed and a temperature produced in excess of that required to vaporise carbon, accompanied by a momentary pressure of 15,000 atmospheres, prove that the failure to produce diamond is not due to lack of temperature. Many of the experiments, in which it has been claimed that diamond is produced, have been repeated, and negative results were obtained unless iron played a part. Experiments under vacua from 75 mm. up to X-ray vacua have shown generally that as the pressure is reduced the yield of diamond is diminished. On the other hand, when alloys, previously boiled under atmospheric pressure, are quickly heated in a high vacuum, violent ebullition takes place, due to the large volume of gases liberated, and some of the contents of the crucible are ejected before

[37] R. J. Meyer, *Zeitsch. anorg. Chem.*, 1914, **86**, 257 ; *A.*, 1914, ii, 369.
[38] L. Rollo and G. Belladen, *Gazzetta*, 1919, **49**, ii, 217 ; *A.*, ii, 34.
[39] (Sir) C. A. Parsons, *Phil. Trans.*, 1919, [A], **220**, 67 ; *A.*, ii, 110.

they have time to part with their occluded gas, and diamond occurs in the spherules so ejected. There is no doubt that these gases, possibly containing a ferro-silicon carbonyl, are necessary for the production of diamond. It seems almost certain that the chief function of quick cooling in the production of diamond in an ingot or spherule is to bottle up and concentrate into local spots the gases occluded in the metal which, under slow cooling, would partly escape, whilst the remainder would become evenly distributed through the mass. The necessity of subjecting the iron to a temperature above 2000° before cooling would imply the necessity of carbides of silicon, magnesium, etc., being present to ensure the necessary chemical reactions with the gases at high pressure within the ingot. The greatest percentage of diamond was obtained when the atmosphere round the crucible consisted of 95 per cent. of carbon monoxide, 1 per cent. of hydrogen, 2 per cent. of hydrocarbons, and 2 per cent. of nitrogen. The weight of diamond was about 1/20,000 that of the iron. It seems probable that the rate of cooling might be so prolonged as to obtain much larger crystals and a larger total yield.

The presence of crystals of SiO_3, Al_2O_3, and MgO, the spinels, and pyrope, associated with diamond in rapidly cooled iron alloys, appears to have a bearing on the presence of similar crystals found in association with diamond, and to be compatible with Bonney's view that eclogite is the parent rock of the diamond in South Africa. It seems probable that both the eclogite and the diamond may have been simultaneously crystallised from an iron alloy. Since the average weight of diamond in the blue ground of South Africa is 1 in 5,400,000, there has been produced in cooled iron more than 270 times this amount.

Investigations were made during the war of the absorptive power of various vegetable charcoals and the improvement that is caused by heat treatment. These have now been published in part, and in the first paper the effect of heat treatment on the absorptive power of sugar charcoal for sulphur dioxide is described.[40] After heating the charcoal for forty-five hours the amount of sulphur dioxide absorbed per gram was increased from 97 c.c. to 288 c.c. In a second paper exactly analogous results were obtained, and a possible explanation is suggested.[41] The main experiments were carried out with birch-charcoal, but other wood charcoals were used. The absorptive powers were measured with sulphur dioxide, carbon dioxide, and also aqueous solutions of methylene blue. It was found that the absorptive power is very materially increased by

[40] R. M. Winter and H. B. Baker, *T.*, 1920, **117**, 319.
[41] J. C. Philip, S. Dunnill, and (Miss) O. Workman, *ibid.*, 362.

the heat treatment, with the result that the activity of animal charcoal can be paralleled and even surpassed by wood charcoal.

It was noticed that the heat-treatment is not the only factor in enhancing the activity, and the clue was found in the decrease in the bulk density of the charcoal during the heating process. If the heating is carried out in the absence of oxygen little or no improvement in the activity is produced, and oxygen must be present for the activation to take place. The explanation is probably that in the case of a freshly prepared sample the capillaries through the material are exceedingly small, so that they are soon blocked when absorption takes place. When the charcoal is heated in the presence of oxygen some oxidation takes place, and the capillaries become wider, so that the effective surface is enormously increased.

A convenient method has been described for the removal of carbon monoxide from its mixtures with other gases for analytical and hygienic purposes.[42] The carbon monoxide is very rapidly oxidised by chromic acid solution to which some mercuric oxide has been added.

Some further work on the derivatives of the silicon hydrides may be reported.[43] It was previously shown that dibromomonosilane reacts with water to form polymerides of protosiloxane, $O \cdot SiH_2$. The unimolecular form has now been obtained as a gas by the action of the required amount of water-vapour on dichloromonosilane in a very large flask under greatly reduced pressure. The compound has an extraordinary tendency to polymerise, in consequence of which the flask must be perfectly clean and smooth. Liquid and solid polymerides are formed immediately on condensation. The liquid ones are like benzene, and can be conveniently obtained as a solution by shaking a benzene solution of dichloromonosilane with water. They correspond approximately with the formula $(SiH_2O)_6$. The solid polymerides are insoluble. All the polymerides react with sodium hydroxide in accordance with the equation $SiH_2O + 2NaOH = Na_2SiO_3 + 2H_2$.

The behaviour of disilane, Si_2H_6, towards halogen acids has been investigated, and is found closely to resemble that of monosilane. Disilane does not appear to react yith hydrogen chloride at the ordinary temperature or at 120°, but in the presence of a little sublimed aluminium chloride a reaction occurs more or less readily accordng to the general scheme :

$$Si_2H_6 + xHCl = Si_2H_{6-x}Clx + xH.$$

A mixture of chlorides is invariably produced, the equilibrium lying

[42] K. Hofmann, *D.R.-P.* 307614 ; *A.*, ii, 309.
[43] A. Stock and K. Somieski, *Ber.*, 1919, **52**, [B], 1851 ; 1920, **53**, [B], 759 ; *A.*, ii, 31, 429.

in favour of the intermediate members of the series. Thus with hydrogen chloride (1 vol.) and disilane (less than 1 vol.) the main product is dichlorodisilane, very little monochlorodisilane being obtained. With the gases in the volume ratio 2:1 much trichlorodisilane, in addition to dichlorodisilane, is obtained. Complete chlorination is not effected by a large excess of hydrogen chloride. It was not found possible to isolate monochlorodisilane in a pure state, and also the final purification of dichlorodisilane could not be effected, since it forms a mixture of constant boiling point with trichlorodisilane. There is no doubt that as in the case of the carbon compounds mixtures of isomerides are formed in the halogenation of disilane.

The bromination of disilane has been carried out in a precisely analogous manner, and monobromodisilane, m. p. $-100°$ to $-101°$, has been isolated in a state of purity.

The hydrolysis of the halogenated disilanes corresponds exactly with that of the similar monosilanes. Thus monobromodisilane reacts with water to yield the substance $(Si_2H_5)_2O$, a colourless liquid which can be volatilised without decomposition, and, when dissolved in benzene, instantaneously reduces cold silver nitrate, but not copper sulphate, solution. It reacts slowly, but quantitatively, with sodium hydroxide solution in accordance with the equation $(Si_2H_5)_2O + 8NaOH + 3H_2O = 4Na_2SiO_3 + 12H_2$. The solid products obtained by the hydrolysis of dibromodisilane and the more highly halogenated derivatives closely resemble silico-oxalic acid, $(HO_2Si \cdot SiO_2H)x$. They are only slowly hydrolysed further by water, can be dried in a desiccator without marked decomposition, evolve hydrogen when treated with alkali hydroxide, and finally yield a residue of silicate. Evidently the Si–Si linking remains intact in them, and appears to be more stable towards alkali than was at first thought.

Amorphous zirconium may be obtained from potassium zirconium fluoride by means of sodium or aluminium, and the coherent form can be prepared from the same salt by aluminothermic reduction.[44] The coherent metal is much less chemically active than the amorphous variety, and, unlike the latter, is insoluble in all acids except hydrofluoric acid and aqua regia.

It has been shown that zirconium monoxide does not exist, the black powders obtained by the reduction of the dioxide by magnesium being mixtures of the metal and the dioxide.[45]

The iodates, perchlorates, and a chlorate have been prepared of

[44] J. W. Marden and M. N. Rich, *J. Ind. Eng. Chem.*, 1920, **12**, 651   *A.*, ii, 547.

[45] R. Schwarz and H. Deisler, *Ber.*, 1919, **52**, [B], 1896 ; *A.*, ii, 42.

zirconium.[46] The following are described: $ZrO(OH)_2,2ZrO(IO_3)_2$, $5ZrO(OH)_2,8ZrO(IO_3)_2$, $3ZrO(OH)_2,4ZrO(IO_3)_2$, $2ZrO(OH)_2,ZrO(IO_3)_2$, $3ZrO(OH)_2,ZrO(IO_3)_2$, $ZrO(ClO_4)_2,HClO_4$, $ZrO(OH)_2,9ZrO(ClO_4)_2$, and $ZrO(OH)_2,3ZrO(ClO_3)_2$.

Following the method described in last year's Report for the preparation of bismuth hydride, tin hydride has also been pre-pared.[47] It is a gas that can be condensed by liquid air and volatilised without decomposition. Some preliminary experiments seem to show that lead hydride also can exist in the gaseous state.

Group V.

Investigations have been made of the electrolysis of a solution of ammonium azide in liquid ammonia at $-67°$ with anodes of various metals.[48] The evolved gases were measured, and the loss of weight of the anode determined. Proof was obtained of the formation of the following azides: CuN_3, CuN_6, AgN_3, CdN_6, PbN_6, and SbN_9. A deep red solution of ferric azide, FeN_9, was obtained, but the compound was ammonolysed, and yielded an ammono-basic ferric azide.

The equilibrium between nitric oxide and bromine and their reaction products has been studied between $-15°$ and $330°$. With bromine at pressures below 50 mm. and at temperatures above $140°$, nitrosyl bromide is formed, the amount of the tribromide present being negligible.[49] Independent evidence of the existence of nitrosyl bromide and nitrosyl tribromide was obtained from the fusion-point diagram. The tribromide, $NOBr_3$, is a brownish-black, almost opaque, liquid, which boils with partial decomposition at $32°$.

It has been found that red phosphorus acts as a reducing agent towards many metallic salts in aqueous solution, and very possibly the method may prove of use in qualitative analysis.[50] The solu-tion of the salt is boiled with $0·2$ gram of red phosphorus for a few minutes. Mercuric and mercurous salts are reduced to the metal, gold and silver salts give insoluble phosphides, whilst, palladium and osmium salts yield either the metal or a phosphide. Stannic salts are partly reduced to stannous salts, ferric salts are

[46] F. P. Venable and I. W. Smithey, *J. Amer. Chem. Soc.*, 1919, **41**, 1722 ; *A.*, ii, 43.

[47] F. Paneth and K. Fürth, *Ber.*, 1919, **52**, [B], 2020 ; *A.*, ii, 41.

[48] A. W. Browne, M. E. Holmes, and J. S. King, *J. Amer. Chem. Soc.*, 1919, **41**, 1769 ; *A.*, ii, 31.

[49] M. Trautz and V. P. Dalal, *Zeitsch. anorg. Chem.*, 1920, **110**, 1 ; *A.*, ii, 308.

[50] L. Rosenstein, *J. Amer. Chem. Soc.*, 1920, **42**, 883 ; *A.*, ii, 428.

reduced to ferrous, iridic salts to iridous, selenates to the element or a phosphide, molybdates to quadrivalent molybdenum salts, vanadates to tervalent vanadium salts, dichromates to chromic salts, and permanganates to manganous salts. Bismuth, lead, cadmium, antimony, and arsenic salts, arsenates, and stannous salts are not reduced, whilst tellurates and platinichlorides are very slowly reduced.

When a few drops of phosphorus trichloride are added to an aqueous solution of arsenious oxide, the solution turns yellow, then opaque-brown, and finally a copious precipitate of arsenic is thrown down.[51] The reaction probably takes place in accordance with the equation $As_2O_3 + 3PCl_3 + 9H_2O = 2As + 3H_3PO_4 + 9HCl$. The arsenic is amorphous, insoluble in carbon disulphide, and is apparently a new allotropic modification. The reaction takes place with arsenates and arsenites, and is very delicate, since the presence of 0·000075 gram of arsenic per c.c. can be detected.

Arsenic trichloride can very conveniently be prepared by passing carbonyl chloride over a mixture of arsenious oxide (80 per cent.) and carbon (20 per cent.) heated at 200° to 260°. The yield is almost quantitative.[52]

Golden antimony sulphide is usually supposed to be a mixture of Sb_2S_5, Sb_2S_3, and some free sulphur. The compound, Sb_2S_5, however, is now shown not to exist, and the golden sulphide, after extraction of the free sulphur, has the formula Sb_2S_4. This sulphide can also be prepared in the following way.[53] By the interaction of Schlippe's salt and zinc chloride, zinc thioantimonate is precipitated. The crude salt contains free sulphur, and, after removal of this, the product has the formula $Zn_3Sb_2S_8$. On treatment with dilute acid, an orange-red residue is obtained, which has the composition Sb_2S_4.

By the oxidation of bismuth oxide or hydroxide in the presence of alkali by chlorine, ammonium persulphate, or potassium ferricyanide, the higher oxides of bismuth have been prepared.[54] The tetroxide was obtained as Bi_2O_4 and Bi_2O_4,H_2O, and of each of these there are two modifications, which are brown and purplish-black respectively. A third variety, $Bi_2O_4,2H_2O$, which is yellow, has also been prepared. Bismuth pentoxide monohydrate, Bi_2O_5,H_2O, is obtained by the oxidation process, but is mixed with the tetroxide. It can be prepared from sodium bismuthate by

[51] N. N. Sen, *J. Proc. Asiatic Soc. Bengal*, 1919, **15**, 263 ; *A.*, ii, 308.
[52] L. H. Milligan, W. A. Baude, and H. G. Boyd, *J. Ind. Eng. Chem.*, 1920, **12**, 221 ; *A.*, ii, 372.
[53] F. Kirchhof, *Zeitsch. anorg. Chem.*, 1920, **112**, 67 ; *A.*, ii, 693.
[54] R. R. Le G. Worsley and P. W. Robertson, *T.*, 1920, **117**, 63.

repeated grinding with glacial acetic acid. The anhydrous oxide does not seem to be capable of existence, as the monohydrate loses both water and oxygen in a vacuum over phosphoric oxide. Bismuth hexoxide has also been prepared by the oxidation process, and is anhydrous.

Group VI.

The solubility has been determined of sulphur dioxide in sulphuric acid of various concentrations.[55] The measurements were carried out at 20°, and the acid concentration was varied from 55 to 100 per cent. It was found that a sharp minimum solubility occurs with an acid containing 86 per cent. of H_2SO_4, and it is significant that the monohydrate, H_2SO_4,H_2O, contains 84·5 per cent. of H_2SO_4.

The oxidation of ferrous chloride in presence of hydrochloric acid, and of ferrous phosphate in the presence of phosphoric acid, by sulphur dioxide has been studied.[56] In the first case, the reaction takes place in accordance with the equation

$$4FeCl_2 + SO_2 + 4HCl = 4FeCl_3 + 2H_2O + S.$$
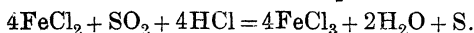
The maximum amount of ferric iron produced was about 9 per cent., and there seems little doubt that the reaction is reversible. In the second case, more ferrous salt is oxidised, and the view is expressed that the reaction

$$4Fe(H_2PO_4)_2 + 4H_3PO_4 + SO_2 = 4Fe(H_2PO_4)_3 + 2H_2O + S$$
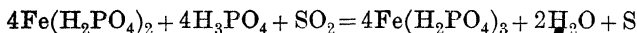
is also reversible, but that it is modified by the formation of the stable complex formed by ferric phosphate and phosphoric acid.

Group VII.

A simple and rapid method has been described for the preparation of iodine pentoxide, which depends on the oxidation of iodine to iodic acid by means of 24—26 per cent. chloric acid solution, the evaporation of the solution, and the dehydration of the iodic acid.[57] The solution of chloric acid is prepared as follows: 625 grams of barium chlorate [90 per cent. $Ba(ClO_3)_2$] are dissolved in 1 litre of nearly boiling water, and the solution is poured into an earthenware crock. The required amount of hot sulphuric acid (obtained by mixing equal volumes of concentrated sulphuric acid and water) was slowly added. It is very necessary to have a slight

[55] F. D. Miles and J. Fenton, T., 1920, 117, 59.

[56] W. Wardlaw and F. H. Clews, ibid., 1093; W. Wardlaw, S. R. Carter, and F. H. Clews, ibid., 1241.

[57] A. B. Lamb, W. C. Bray, and W. J. Geldard, J. Amer. Chem. Soc., 1920, 42, 1636; A., ii, 615.

excess of barium chlorate rather than sulphuric acid, as the latter renders the iodine pentoxide less stable. The solution of chloric acid may be kept unchanged in glass bottles for several weeks. It is found that in the presence of 3 per cent. excess of chloric acid the net reaction with iodine is expressed by the equation

$$I_2 + 2HClO_3 = 2HIO_3 + Cl_2.$$
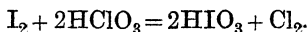
The mechanism of the reaction, however, does not consist of the direct replacement of chlorine by iodine. A considerable quantity of chloric acid is reduced to hydrochloric acid in accordance with the equation $3I_2 + 5HClO_3 + 3H_2O = 6HIO_3 + 5HCl$. A solution containing hydrochloric and iodic acids loses iodine on evaporation according to the equation $2HIO_3 + 10HCl = I_2 + 5Cl_2 + 6H_2O$. This is prevented by an excess of chloric acid, which reacts with the hydrochloric acid, and it was found that an excess of 3 per cent. is sufficient.

The iodine is oxidised in quantities of 500 grams, the reaction being finished in about twenty minutes. The iodic acid obtained on evaporation is heated at 150—160° for three hours. The final dehydration is carried out at 235—240° in a slow current of dry air. The iodine pentoxide is pure white, and has practically the theoretical oxidising value, and the yield is almost quantitative. The process has many advantages over the nitric acid method.

With reference to this preparation of iodic acid, it is interesting to note that iodine replaces bromine when the former acts on an aqueous solution of potassium bromate, and that a similar reaction does not occur with bromine and potassium chlorate, whilst the reaction between iodine and potassium chlorate is more complex.[58] The following changes have been shown to occur:

$$2KClO_3 + 2I + H_2O = KHI_2O_6 + KCl + HClO$$

and $KHI_2O_6 + KCl + HClO = 2KIO_3 + H_2O + Cl_2.$
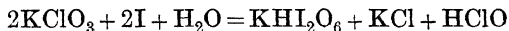
Potassium manganifluoride, K_2MnF_5,H_2O, has been prepared by the action of nitrous acid on potassium permanganate in the presence of hydrofluoric acid.[59] The permanganate is reduced by the nitrous acid. A manganous salt may also be used, in which case the nitrous acid acts as an oxidising agent.

Group VIII.

It has been found that the yield of sodium ferrate obtained by the electrolysis of sodium hydroxide solution with iron anodes is very materially increased by superposing an alternating current

[58] G. Gruber, *Zeitsch. physikal. Chem. Unterr.*, 1920, **33**, 107 ; *A.*, ii, 684.
[59] I. Bellucci, *Gazzetta*, 1919, **49**, ii, 180 ; *A.*, ii, 40.

on the direct current.[60]   In one case the increase of yield was 160 per cent.   If the anode and cathode are separated, and the temperature of the electrolyte is not allowed to exceed 50°, at which the ferrates decompose, and an alternating current is superimposed on the direct current, saturated solutions of sodium ferrate and the crystalline salt can be obtained.

Some further work has been carried out on the influence of hydrogen sulphide on the occlusion of hydrogen by palladium.[61] The earlier experiments were discussed at some length in the Report for last year.   In the earlier paper it was shown that when palladium is poisoned by hydrogen sulphide, and then heated at 100° in a vacuum, an amount of hydrogen is evolved equal in volume to that of the hydrogen sulphide previously absorbed in the poisoning.   The sulphur is retained by the palladium, a complex of the formula Pd_4S being formed.   Dr. Maxted believes that palladium can dissociate hydrogen sulphide to form this complex and free hydrogen slowly at ordinary temperatures.   When this takes place, more hydrogen is slowly occluded, and the total volume so occluded added to the volume derived from the hydrogen sulphide is equal to the true occlusive power of palladium for hydrogen, allowing for the palladium which has formed the Pd_4S complex.   This explanation is based on the observation that a sample of palladium which has been completely poisoned by hydrogen sulphide slowly gains a power of absorbing hydrogen up to a fixed amount, and that the rate of absorption is faster the longer the poisoned palladium is kept before the hydrogen is admitted.

This interpretation may be criticised from two points of view. In the first place, since the palladium dissociates hydrogen sulphide, it is probable that this dissociation occurs at the time of occlusion, and that it is, indeed, the basis of the occlusion.   In the second place, if palladium is absolutely completely poisoned by hydrogen sulphide, it should not gain, on keeping for an unlimited time, any power of occluding hydrogen.   Dr. Maxted offers no explanation of his view that the occlusive power for hydrogen should be increased when the hydrogen sulphide is dissociated.   True poisoning must mean the absorption of hydrogen sulphide up to the point when a portion of the palladium is converted into the complex Pd_4S, and the remainder is saturated with the hydrogen obtained by the dissociation of the hydrogen sulphide.   Obviously, when this has been secured, no further hydrogen can be occluded. It would seem far more probable that the poisoning obtained with

[60] G. Grube and H. Gmelin, *Zeitsch. Elektrochem.*, 1920, **26**, 153 ; *A.* ii, 377.   [61] E. B. Maxted, *T.*, 1920, **117**, 1280.

hydrogen sulphide is not complete in the strict sense, but that the poisoning is concentrated on the surface. On allowing the partly poisoned palladium to remain, a more equal distribution of the hydrogen takes place, with the result that more hydrogen can be occluded. This is shown by the fact that, even after the palladium has been "completely" poisoned by hydrogen sulphide, it still possesses the power of slowly absorbing more hydrogen sulphide.

The data are still too incomplete for accurate calculations of the true equilibrium conditions. It appears that 1 gram of palladium has the definite power of absorbing 69 c.c. of hydrogen. Is the whole of this hydrogen dissociated into atoms, or are there two processes, first the occlusion of hydrogen as atoms, followed by a secondary effect of condensation as hydrogen molecules? The second alternative seems the more probable, but the question can only be decided by accurate measurements of the dissociation pressures of hydrogenised palladium.

An investigation has been made of the hydrolysis of aqueous solutions of potassium platinichloride.[62] It is shown that $N/50$ and more concentrated solutions are slowly and completely hydrolysed in the dark, whilst $N/100$ and more dilute solutions undergo hydrolysis only when exposed to light. It is found that the hydrolysis takes place at first very slowly, but after a time the rate increases, and this is attributed to the formation of some substance which acts as a catalyst. This view was supported by the fact that the addition of a portion of a photochemically hydrolysed solution to a fresh $N/100$-solution of platinichloride causes the latter to undergo hydrolysis in the dark.

The addition of a soluble chloride to the hydrolysed solution causes a complete reversal of the reaction, and this reverse reaction is influenced by light in much the same way as is the direct reaction. The influence of platinum-black in accelerating both the direct and reverse reactions in the dark is quite noticeable, but is not measurable when light is acting on the solutions.

E. C. C. BALY.

[62] E. H. Archibald, *T.*, 1920, **117**, 1104.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

A SURVEY of the literature shows that few laboratories have yet been able to devote much of their energies to systematic research on the pre-war scale. The present Report deals only with such papers as the writer considers of importance from the theoretical point of view or for new methods of preparation. A distinctive feature of this year's literature is the number of papers dealing with the compounds used so extensively in chemical warfare, and with alternative methods for the synthesis of substances of which there was a scarcity in the belligerent countries.

Hydrocarbons.

Very few investigations on hydrocarbons have been described during the year, but it is of interest to gauge the success attending the strenuous efforts made in Mid-Europe to use paraffin for the production of fatty acids and their esters to overcome the shortage of natural fats. The usual method was to heat the hydrocarbons of high molecular weight with oxygen or air, generally under pressure in the presence of a catalyst. Thus, in the presence of manganese compounds, C. Kelber[1] converted a paraffin wax (m. p. 50°), by the action at 150° of a stream of finely divided oxygen, into a mass of which more than 35 per cent. consisted of fatty acids insoluble in water, and about 25 per cent. of the lower (up to C_{10}) fatty acids.

H. H. Franck[2] used also up to 5 per cent. of various compounds of lead, mercury, vanadium, and chromium, and, working at 150° in an autoclave filled with oxygen, obtained from paraffin of lower melting point 40 per cent. of fatty acids of higher, and 57 per cent. of acids of lower, molecular weight. A mixture of the acids so obtained was esterified with ethylene glycol, and yielded an edible fat said to resemble coconut oil. A variation is described

[1] *Ber.*, 1920, **53**, [B], 66, 1567 ; *A.*, i, 280.
[2] *Chem. Zeit.*, 1920, **44**, 309 ; *A.*, i, 417.

by F. Fischer and W. Schneider,[3] who worked in a steel autoclave at 170° in the presence of sodium carbonate, the mixture being stirred by pumping in compressed air. These authors obtained a 90 per cent. yield of fatty acids from crude paraffin, and are of the opinion that iron, copper, and manganese have equal catalytic effects. A. Grün[4] has studied these reactions more in detail, and shown that the results are dependent on many factors as yet little understood. In the absence of water the anhydrides of the higher fatty acids are formed, and in every case the neutral products contain ketones, such as stearone. The acids formed all appear to have a "straight-chain" structure, whilst, according to Fischer and Schneider, the acids containing an uneven number of carbon atoms are formed in greater quantity than those with an even number, which are commonly derived from natural fats.

The list of compounds formed in the pyrogenic condensation of acetylene has been considerably increased[5] by the crystallisation of the picrates of the higher boiling fractions of the tar. It has been shown[6] that acetylene condenses at 100—200° with methane in the presence of metallic catalysts, giving a 70 per cent. yield of propylene; at higher temperatures (200—350°), non-metallic catalysts, such as thoria and silica, give similar results[7] even with at least the lower homologues of both acetylene and methane.

The importance of a study of the mercury compounds of acetylene was emphasised in last year's Report, and attention should be drawn to the theoretical discussion by W. Manchot and A. Klüg[8] of those of ethylene and of carbon monoxide. A detailed study of the conversion of acetylene into acetaldehyde and into acetic acid in the presence of mercury catalysts is described by B. Neumann and H. Schneider.[9] The best yield (90 per cent.) of acetaldehyde was obtained when the gas was led with vigorous mechanical stirring into a catalyst composed of 96 per cent. acetic acid, containing 3 per cent. of mercuric sulphate, the temperature being maintained at about 30°. The best results (83 per cent. yield) in the direct conversion of acetylene into acetic acid were obtained by using the same catalyst, with the addition of vanadium pentoxide, acetylene and oxygen being led in alternately.

[3] *Ber.*, 1920, 53, [B], 922 ; *A.*, i, 519.   [4] *Ibid.*, 987 ; *A.*, i, 518.
[5] R. Meyer and K. Taeger, *ibid.*, 1261 ; *A.*, i, 589.
[6] A. Heinemann, *D.R.-P.* 315747 ; *A.*, i, 281.
[7] Chemische Fabrik Buckau, *D.R.-P.* 294794 ; *A.*, i, 657.
[8] *Annalen*, 1920, 420, 170 ; *A.*, i, 720 ; also *Ber.*, 1920, 53, [B], 984 ; *A.*, i, 519.
[9] *Zeitsch. angew. Chem.*, 1920, 33, 189 ; *A.*, i, 657.

Alcohols and their Derivatives.

In the catalytic reduction of acetaldehyde by hydrogen, the production of ethyl alcohol falls off gradually with the formation of ethyl ether as a by-product, whilst the catalyst is poisoned by decomposition products of acetaldehyde. These undesirable results are avoided [10] by the use of an excess of hydrogen containing about 0·2 per cent. of oxygen, and when working between 90° and 170°, at which temperature acetaldehyde begins to decompose, a yield of 95 per cent. of alcohol can be obtained. The beneficial effect of the oxygen cannot, however, be wholly attributed to the oxidation of carbon monoxide or other impurities, to the presence of which the injurious effect on the catalyst has been ascribed. If hydrogen quite free from oxygen be used (and it is stated that electrolytic hydrogen invariably contains some oxygen), a mixture of alcohol and ether is produced. The formation of ether commences at about 90°, and in the process up to 15 per cent. is obtained.

The formation of acetone by the fermentation of starch is dependent as a commercial process on the utilisation of the n-butyl alcohol, of which at least two parts are produced for every one of acetone.[11] In this connexion the transformation of the alcohol into methyl ethyl ketone is promising,[12] as the various reactions proceed quite smoothly. These are: The catalytic dehydration of the alcohol by glacial phosphoric acid at about 350°, the absorption of the β-butylene (freed from γ-butylene by scrubbing with 60 per cent. sulphuric acid) in concentrated sulphuric acid, formation of sec.-butyl alcohol by the action of water on the butyl hydrogen sulphate thus produced, and the catalytic dehydrogenation by copper of the sec.-butyl alcohol by the Sabatier and Senderens process. The use of n-butyl alcohol as a starting material for various synthetical reactions, such as the preparations of n-amyl alcohol, n-valeric and n-hexoic acids, has been studied by R. Adams and C. S. Marvel.[13] The writer can recommend their methods, which give very good yields and are well adapted for students' exercises in place of some of the preparations usually set.

Further condensations of n-butyl alcohol with the corresponding aldehyde,[14] and of n-butyl chloroformate [15] with alcohols and

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[10] Elektrizitätswerk Lonza, *Brit. Pat.* 134521; *D.R.-P.* 317589; *A.*, i, 134.
[11] J. Reilly, W. J. Hickinbottom, F. R. Henley, and A. C. Thaysen, *Biochem. J.*, 1920, **14**, 229; *A.*, i, 465.   [12] A. T. King, *T.*, 1919, **115**, 1404.
[13] *J. Amer. Chem. Soc.*, 1920, **42**, 310; *A.*, i, 283.
[14] C. Weizmann and S. F. Garrard, *T.*, 1920, **117**, 324.
[15] F. D. Chattaway and E. Saerens, *ibid.*, 708.

amines, according to well-known reactions have also been described. A. Mailhe and F. de Godon [16] have continued their studies of the catalytic preparation of ethers in the dry way, and recommend aluminium oxide (prepared by heating commercial ammonium alum at 190°) as a catalyst. This method gives about 70 per cent. of diethyl ether from 96 per cent. alcohol, and is suitable for the preparation of simple and mixed aliphatic ethers containing normal groups, but fails with *iso*propyl and *iso*butyl alcohols, and gives only a 30 per cent. of the corresponding ether from allyl alcohol.

The catalytic effect of mineral acids in esterification is attributed to their linking the alcohol and organic acid in a molecular complex, where opportunity is afforded for an interchange of radicles. While investigating this, O. Maass and J. Russell [17] have proved the existence of an oxonium compound, $(C_2H_5)_2O,HBr,H_2O$, but could not obtain definite evidence of a compound of ether, hydrogen bromide, and ethyl alcohol. Very similar suggestions are made by O. Aschan,[18] who explains the catalytic effect of ether in aiding the addition of hydrogen chloride and of sulphuric acid to unsaturated compounds as due to the intermediate formation of diethyloxonium salts. He shows that the mixing of ether and sulphuric acid monohydrate causes a large development of heat, and gives a mixture more viscous than the sulphuric acid, but he was unable to isolate the diethyloxonium sulphate or any of its salts.

Lowry and co-workers [19] describe experiments to recover the oxidised nitrogen in cordite in the form of calcium nitrate. They consider that hydrolysis of the normal type is not the predominant action when cordite is decomposed by lime in the presence of pyridine. The calcium salt of hydroxypyruvic acid is an important product of the reaction, and these authors suggest that the main action is a decomposition of the nitric ester into a ketone or aldehyde and a nitrite. R. C. Farmer,[20] however, from a review of their work and that of the numerous previous workers at this problem, and from some fresh experimental data on the decomposition and hydrolysis of glyceryl nitrates, disagrees with their conclusions and, tracing the various stages of the different forms of decomposition of nitric esters, maintains that the first stage in such is a true ester hydrolysis of the normal type.

[16] *Bull. Soc. chim.*, 1919, [iv], **25**, 565; 1920, [iv], **27**, 121, 328; *A.*, i, 6, 284, 470. •
[17] *Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 259; *A.*, i, 521.
[18] *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, No. 8; *A.*, i, **136**.
[19] T. M. Lowry, K. C. Browning, and J. W. Farmery, *T.*, 1920, **117**, 552.
[20] *Ibid.*, 806.

Aldehydes and Ketones.

The oxidation of methyl alcohol to formaldehyde has been investigated by many workers in the past, but the latest contribution to the subject is valuable. In this, M. D. Thomas[21] compares the relative catalytic effect on the oxidation under different conditions of silver, gold, and copper. Of these, silver has the best effect, and by its use a yield of more than 55 per cent. was obtained in the process. Finely divided silver,[22] preferably deposited on asbestos, is recommended also for the catalytic oxidation by air at about 250° of primary and secondary alcohols to the corresponding aldehydes and ketones. The action tends to become very intense owing to rise of temperature of the catalyst, but if care be taken to regulate this, the method can be employed generally with success even with unsaturated alcohols.

A new and in some cases a very useful method of preparing aldehydes is patented by C. Harries,[23] who shows that ozonides can be reduced preferably by ferrocyanides to aldehydes, nonaldehyde, for example, being formed by the reduction of the ozonide of oleic acid.

The great diversity in the type of compounds which acetylacetone forms with metals, metalloids, and non-metals has now been extended by the discovery of a new type in the selenium and tellurium acetylacetonates, which are described in a paper[24] bearing on the complex questions of residual affinity and co-ordination.

An attempt[25] to use the additive compounds of the acetylacetonates of the metals of the rare earths with ammonia and amines as a convenient means of separating these elements was, however, quite unsuccessful.

Acids and their Derivatives.

Very little work in this section has been published during the year. The details[26] of a much improved method of preparing gluconic acid on a technical scale suggest that this may be utilised as a substitute for some of the more expensive vegetable acids.

[21] *J. Amer. Chem. Soc.*, 1920, **42**, 867 ; *A.*, i, 473.

[22] C. Moureu and G. Mignonac, *Compt. rend.*, 1920, **170**, 258 ; *A.*, i, 283.

[23] *D.R.-P.* 321567 ; *A.*, i, 675.

[24] G. T. Morgan and H. D. K Drew, *T.*, 1920, **117**, 1456.

[25] G. Jantsch and E. Meyer, *Ber.*, 1920, **53**, [B], 1577 ; *A.*, i, 711.

[26] A. Herzfeld and G. Lenart, *Zeitsch. Ver. deut. Zuckerind.*, 1919, 122 ; *A.*, i, 143.

The well-known work of K. Meyer and co-workers on the keto-enolic desmotropy of the esters of β-ketonic acids has been extended[27] to an examination of the effect of fractional distillation on ethyl acetoacetate. By the use of Jena-glass apparatus, which had been steamed and washed with alcoholic hydrogen·chloride, it has been found possible to isolate the less volatile ketonic form by distillation under a pressure of 2 mm. The proportion of enol to ketone is unaffected by distillation, for the actual amounts of the two forms in the original ester before distillation in a quartz vessel and in three fractions and a residue, all of equal volume, were practically the same, whilst the residue was free from the enolic form. The method obviously affords the easiest means of preparing the pure ketonic ester, and by repeated distillation of large amounts of the ester might yield the pure enolic form. Similar results are recorded for the distillation of methyl benzoylacetate, although the fractionation proceeds more slowly, but with this ester a small first fraction solidified to give the pure enolic form. For many years it has been the practice to postulate the existence of enolic forms of aliphatic esters to explain certain reactions. H. Scheibler and J. Voss[28] have shown that the potassio-derivatives of esters, which contain at least one hydrogen atom attached to the carbon atom in the α-position with respect to the carbalkyloxy-group, are readily obtained as coloured amorphous substances when an ethereal solution of the ester is added to the• finely divided metal, which is covered with ether heated to gentle ebullition; under these conditions the metal dissolves immediately with evolution of hydrogen, whilst the metallic derivative remains more or less completely in colloidal solution in ether. Sodium acts less energetically, and the corresponding derivatives are often only formed at temperatures at which they are partly decomposed. These ester-enolates are very unstable substances, which can, however, be preserved for some time under ether in an atmosphere of hydrogen or nitrogen. They are immediately decomposed on the addition of water with the regeneration of the esters, but react with carbon dioxide, giving colourless potassium salts of carboxylic acids, which are stable towards oxygen and water, but contain the carboxylic group in a very loose state of combination. So far not much evidence has been brought forward to prove the formulæ ascribed to these compounds, but the reaction between ethyl chloroformate and ethyl potassio-acetate can be to some extent explained on the basis of the formula $CH_2{:}C(OK){\cdot}OEt$.

Many difficulties are met with when attempts are made to syn-

[27] K. H. Meyer and V. Schoeller, *Ber.*, 1920, **53**, [B], 1410; *A.*, i, 707.

[28] *Ibid.*, 388; *A.*, i, 366.

thesise the natural fats. Up to the present the general methods for the preparation of mono- and di-glycerides have depended either on the action of glyceryl chlorohydrins on the salts of fatty acids or on esterification of the fatty acid with the chlorohydrin, and the subsequent exchange of the halogen atoms for the hydroxyl group. Now the glyceryl monochlorohydrins [29] are difficult to prepare in a state of purity, and are not adapted for such synthetical reactions, as these methods are complicated by side-reactions. There is, further, no guarantee of the simple replacement of the halogen by the acyl radicle, whilst, in fact, several instances of the wandering of such acyl groups are now known.[30] A new method, which will yield α-monoglycerides of undoubted purity, is published [31] under the names of Emil Fischer and co-workers. As initial material " acetone glycerol " is used, and the constitution of this has been shown by Irvine, Macdonald, and Soutar [32] to be

isopropylideneglycerol, $\quad CMe_2 \!<\! \begin{matrix} O \cdot CH_2 \\ O \cdot CH \cdot CH_2 \cdot OH \end{matrix}$. This compound

reacts readily in the presence of quinoline with acid chlorides, yielding products from which the acetone residue is easily removed by dilute acids at about 50°, thus giving undoubted α-monoglycerides. The results of this important work throw great suspicion on the purity of the monoglycerides previously described, whilst it may be expected that the method, even without the guiding hand of Fischer, will lead to further knowledge of the chemistry of fats.

Halogen Compounds.

One of the less pleasant features of the literature this year is the large amount of space which has been devoted to descriptions of various halogen compounds used so extensively in chemical warfare. The preparation and properties of $\beta\beta'$-dichlorodiethyl sulphide have been detailed in the chemical journals of five countries, in the allied countries it having been made very simply by the action [33] of sulphur monochloride on ethylene at about 60°, whilst in Germany the more complicated synthetic process through ethylene chlorohydrin and $\beta\beta'$-dihydroxydiethyl sulphide was used as described by Victor Meyer in 1886. Several chemists have used the highly reactive dichlorosulphide for various synthetical

[29] L. Smith and E. Samuelson, Zeitsch. physikal. Chem., 1920, 94, 691 ; A., i, 658.

[30] E. Fischer, Ber., 1920, 53, [B], 1621 ; A., i, 808.

[31] E. Fischer, M. Bergmann, and H. Bärwind, ibid., 1589 ; A., i, 805.

[32] T., 1915, 107, 337.

[33] (Sir) W. J. Pope, C. S. Gibson, and H. F. Thuillier, Brit. Pat. 142875 ; A., i, 523.

experiments, of which perhaps the most complete account is that by O. B. Helfrich and E. E. Reid.[34]

French chemists [35] have made very detailed studies of the numerous compounds produced by the substitution of hydrogen by chlorine in methyl formate and carbonate; it may be expected that some of these will be of considerable use in synthetical work.

A very convenient modification of the older methods of preparing alkyl bromides is described by O. Kamm and C. S. Marvel.[36] In this a solution of hydrobromic acid is first prepared by the reduction of bromine by sulphur dioxide in the presence of water. Concentrated sulphuric acid is then added, and the mixture heated under a reflux with the alcohol to be brominated. The method can be recommended, as it gives good yields with very little trouble.

$\alpha\beta$-Dichlorovinyl ethyl ether is readily prepared from the commercial trichloroethylene by the action of sodium ethoxide, and has been found useful in the synthesis of chloroacetates and acid chlorides.[37]

Numerous new per-iodides of carbonyl compounds [38] and esters [39] have been described, and it is remarkable that those prepared from diethyl oxalate of the type $(C_2O_2Et_2)_4,NaI,I_4$ were obtained in the presence of water. These compounds are apparently oxonium derivatives, and will require consideration from those studying residual valency.

Optical Activity.

It has been well known in a few cases that the taste of some optically active compounds is different from that of their optical antipodes. This very difficult field of research has not received much attention, and an interesting paper [40] on the relative sweetness of some compounds of α-hydroxy*iso*hexoic or "leucic" acid is all the more welcome. It is a common practice in Japan to use certain amino-acids, such as *d*-glutamic acid and its salts, as taste-producing substances in food, and the author, by replacing the amino-group in some of these by hydroxyl, has obtained some very sweet substances. Thus, by suitable treatment, leucine has been converted into the corresponding hydroxy-acid. The sodium, ammonium, potassium, and calcium salts are very sweet, the sodium

[34] *J. Amer. Chem. Soc.*, 1920, **42**, 1208 ; *A.*, i, 524.

[35] *Inter alia*, V. Grignard, G. Rivat, and E. Urbain, *Compt. rend.*, 1919, **169**, 1143 ; *A.*, i, 138.

[36] *J. Amer. Chem. Soc.*, 1920, **42**, 299 ; *A.*, i, 282.

[37] H. Crompton and (Miss) P. L. Vanderstichele, *T.*, 1920, **117**, 564.

[38] A. M. Clover, *J. Amer. Chem. Soc.*, 1920, **42**, 1248 ; *A.*, i, 528.

[39] A. Skrabal and E. Flach, *Monatsh.*, 1919, **40**, 431 ; *A.*, i, 527.

[40] S. Kodama, *J. Tokyo Chem. Soc.*, 1919, **40**, 825 ; *A.*, i, 471.

salt being about ten times as sweet as sucrose. The taste is apparently due to the α-hydroxy*iso*hexoic ion, since all the salts and the acid itself in dilute solution are sweet, whilst the solid acid and its ester are not. It is remarkable that the two anhydrides of leucic acid with the formulæ $C_4H_9 \cdot CH <^{CO \cdot O}_{O \cdot CO}> CH \cdot C_4H_9$ and $C_4H_9 \cdot CH(OH) \cdot CO \cdot O \cdot CH(CO_2H) \cdot C_4H_9$ are bitter, but become sweet when boiled with dilute alkalis. The acetyl and alkyl derivatives of the leucic acid are not sweet, and their salts are tasteless, but a salt of acetyl-leucic acid when boiled with water slowly becomes sweet, owing to the elimination of the acetyl group. The sweetness of d-glutamic acid is twice as great as that of the dl-acid, and the sweetness of a salt of leucic acid depends on the amount of the dextrorotatory form which is present. Thus, having obtained by a Walden inversion a dextrorotatory leucic acid from the corresponding l-acid, the author shows that the salts of the d-acid are sweeter than those of the dl-acid, which are also sweeter than those of the l-acid.

Some years ago Hudson suggested that the difference between the molecular rotations of the α- and β-forms of mutarotatory sugars is a constant, and afterwards extended these views [41] to the phenylhydrazides of certain acids of the sugar group. He succeeded in showing that in acids containing α-, β-, γ-, and δ-asymmetric carbon atoms, the rotation due to the α-carbon atom was very much larger than the values due to the other three carbon atoms added together, and so the direction of the rotation of the phenylhydrazide could be used as an indication of the configuration of the hydroxyl group attached to the α-atom. His results have now received valuable confirmation from the extended investigation of Mlle. T. W. J. van Marle,[42] who, working with gluconic, mannonic, galactonic, gulonic, idonic, *iso*saccharic, arabonic, ribonic, xylonic, and lyxonic acids, has been able to prove that Hudson's conclusions hold equally in aqueous solution for the hydrazides, p-bromophenylhydrazides, o-, m-, and p-tolylhydrazides, the amides, anilides, and o-, m-, and p-toluidides. It is not surprising, however, that conflicting results were obtained when the rotations of these compounds were examined in pyridine solution, and in the opinion of the writer it seems a great pity, in view of the results obtained in recent years in the domain of optical activity, that the material prepared with so much trouble for this research was not examined with monochromatic light of more than one wave-length.

[41] *J. Amer. Chem. Soc.*, 1917, **39**, 462 ; *A.*, 1917, i, 318.

[42] *Rec. trav. chim.*, 1920, **39**, 549 ; *A.*, i, 592.

The hydrolysis of the esters of certain optically active hydroxy-acids has yielded in the past very perplexing results, and a summary[43] of the behaviour on hydrolysis of the optically active menthyl and bornyl esters of the various isomeric "phenyl-lactic" and other acids is welcome. Mandelic acid and tropic acid,

$$C_6H_5 \cdot CH(CH_2 \cdot OH) \cdot CO_2H,$$
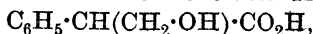
are racemised readily, and their esters are catalytically racemised by warming with an amount of alcoholic solutions of sodium or potassium hydroxide insufficient to complete the hydrolysis; on the other hand, the acids $C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot CO_2H,$

$$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H,$$
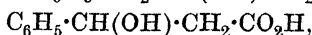
and $C_6H_5 \cdot CMe(OH) \cdot CO_2H$, and their esters, are far less prone to racemisation. Thus it appears that although compounds of the type $R \cdot CH(OH) \cdot CO_2R'$ present a system prone to racemisation in virtue of the mobile hydrogen atom being in the α-position, this circumstance is not in itself a factor in promoting racemisation unless R is an aromatic residue attached directly to the asymmetric atom. In the event of R being an aliphatic group, it may be argued that this system would probably be stable, so far as race-misation by alkali is concerned, and this is confirmed to some extent by experiments with lactic acid.

C. Neuberg and F. F. Nord[44] have investigated the phyto-chemical reduction of unsymmetrical ketones. These, added to sucrose undergoing fermentation by yeast, are partly reduced to secondary alcohols. The hydrogenation does not proceed at all readily, but the diastereoisomerides are formed at different rates, so that the products, whilst not optically pure, have a considerable activity, which is much greater than observed by Le Bel in his classical experiments on the preferential decomposition by moulds of the diastereoisomerides of secondary alcohols. They claim also to prepare a lævorotatory $\beta\gamma$-butylene glycol by the hydrogenation of diacetyl by similar means, a result which is all the more remark-able as previous investigators have found that the production of the glycol from carbohydrates by bacterial agency leads only to the racemic or *meso*-forms.

An interesting attempt[45] has been made to summarise the phenomena observed among the optically active substances found in the animal and plant kingdoms. Whilst there are several exceptions, it would appear that, in general, the normal products of animal metabolism occur in optically active forms, but in the case of the plant organism, on the other hand, the diastereo-

[43] A. McKenzie and H. Wren, *T.*, 1920, **117**, 680.

[44] *Ber.*, 1919, **52**, [B], 2237, 2238; *A.*, i, 135.

[45] K. Hess and W. Weltzien, *ibid.*, 1920, **53**, [B], 119; *A.*, i, 328.

isomerides are not infrequently formed in equal amounts. It is probable, however, that the specific action of an enzyme is only conditional, and that whilst a ferment appears to attack preferentially one modification of a given compound, it can, in case of necessity, attack the antipode, or it may be that whilst under normal conditions the rate of reaction between an enzyme and the two diastereoisomerides is different, when the conditions are suitable the rate becomes identical. The production of optically inactive bases containing an asymmetric carbon atom may be ascribed, however, to other causes. Thus, racemisation of a primarily formed optically active alkaloid may have occurred during the treatment of the dead plant with extracting solvents, or it may have occurred within the plant during its life, or, again, the formation of the alkaloid in the living plant may have been brought about by ordinary symmetrical forces in which enzymes have no part. It is well known, however, that alkaloids vary very greatly in their resistance to racemising reagents; thus hyoscyamine is readily converted by alkalis into atropine, and pelletierine and allied substances are less prone to racemisation in this way, whilst coniine and d-methylconiine are unchanged by drastic treatment with acids or alkalis.

E. Erlenmeyer [46] has described the formation of optically active cinnamic acids. It is suggested that the activation of the cinnamic acid is brought about by the "induction" influence of other optically active components involved in the reactions. Thus when an optically active phenylbromolactic acid is reduced with zinc in hot alcoholic solution, one half of it passes into phenyl-β-lactic acid and the other half into cinnamic acid, which has a rotation of the same sign as that of the bromo-acid. The activity of the resulting cinnamic acid is not due to contamination with phenyl-lactic acid, as repeated extractions with water still leave an active cinnamic acid, and this is further confirmed by comparative experiments with actual mixtures of optically inactive cinnamic acid and active phenyl-lactic acid. In a similar manner, a lævorotatory dibromide of cinnamic acid is formed by the action of bromine on a mixture of the zinc salts of cinnamic and d-phenyl-lactic acid, an opposite result being obtained when l-phenyl-lactic acid was used. The reduction products of l- and of d-phenylbromolactic acids in the same way yield dibromides of cinnamic acid with rotations opposite in sign to that of the bromo-acids employed. Further experimental results obtained are: cinnamic acid "activated" under the influence of l-mandelic or l-chlorosuccinic acid becomes dextrorotatory and yields a lævorotatory dibromide, whilst with d-tartaric

[46] *Biochem. Zeitsch.*, 1919, **97**, 198 ; *A.*, i, 45.

acid or with *d*-cinchonine, a lævorotatory acid and dextrorotatory dibromide are formed.

As the geometrical isomeric formula of cinnamic acid with the double bond cannot account for the active cinnamic acids, the author suggests a stereoisomeric structure with free unsaturated affinities, thus:

and   instead of
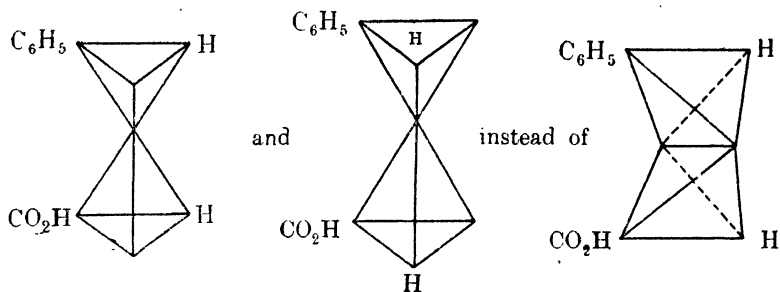
Recent work by Lowry and others has stimulated a re-examination of the menthyl esters of certain keto-acids described previously by Rupe [47] and his co-workers. The rotations of these were observed only for sodium light, but light of other wavelengths has now been used. Most of these substances are not, however, homogeneous, containing varying proportions of the enolic and ketonic forms, according to the conditions. However, the authors "re-discover" the applicability of a one-term Drude equation, $a = k/\lambda^2 - \lambda_0^2$, as has been shown by Lowry and other investigators, to the optical dispersion of a great number of compounds. They adopt the following classification of abnormal rotatory dispersion: (i) total anomaly of a mixture of two substances with opposed activities (Tschugaev's extramolecular anomalous dispersion); (ii) total anomaly of a compound containing two different asymmetric complexes, one of which is dextro-, the other lævo-rotatory (Tschugaev's intramolecular anomalous dispersion); (iii) when the rotatory dispersion curve does not pass through a maximum or minimum, neither does it approximate to a horizontal line, but λ and λ_0^2 differ widely from the normal values and $\dfrac{1}{a}\Big/\lambda^2$ gives bent or zig-zag lines (complex rotatory dispersion of Lowry); (iv) apparently normal course of the curves and $\dfrac{1}{a}\Big/\lambda^2$ gives straight lines, but λ_a and λ_0^2 differ greatly (at least $\pm 15\,\mu\mu$ for the former) from the normal value for the particular class of compound (relative anomaly).

[47] H. Rupe and H. Kägi, *Annalen*, 1920, **420**, 33; *A.*, i, 748.

The paper contains a criticism of the proposal by Lowry and Abram [48] to delete the "relatively abnormal" classification; the authors consider that sufficient substances are known, in which λ_a differs by 15—60 $\mu\mu$ and $\lambda_0{}^2$ by as much as five units from the normal figures for the class of substance without, however, exhibiting complex anomaly, to justify a separate classification.

It may be pointed out, however, that many substances have rotations which are numerically low, whilst the accuracy of the determination of rotatory power is not very great, so that in the opinion of the writer it is unwise in the present state of knowledge to adopt the more elaborate classification set out by Rupe.

Carbohydrates and their Derivatives.

In 1913 Emil Fischer [49] obtained a strongly reducing compound, $C_6H_{10}O_4$, which he named glucal, by the reduction of β-acetobromo-glucose with zinc dust and acetic acid. It is a slightly sweet, soluble, viscid syrup with aldehydic properties, and evidently possesses ethylenic unsaturation, since it decolorises bromine water. When hydrogenated in the presence of palladium, hydroglucal is formed, and this contains no double bond; the same product is formed if the acetate of glucal is similarly hydrogenated and then hydrolysed. The constitution of glucal has not been conclusively proved, but the latest paper [50] shows that its properties are satisfactorily explained by the formula •

$$\text{OH·CH}_2\text{·CH(OH)·CH·CH(OH)·CH:CH.}$$
$$\underset{\text{————O}}{|\qquad\qquad\qquad|}$$
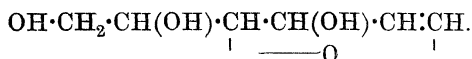
New reactions pointing to this formula are: (a) the additive product of glucal and bromine, when treated with silver acetate, yields a stereoisomeric mixture of tetra-acetylglucose-β-bromohydrins, $\text{OAc·CH}_2\text{·CH(OAc)·CH·CH(OAc)·CHBr·CH·OAc}$, which, after
$$\underset{\text{————O————}}{|\qquad\qquad\qquad\qquad|}$$
deacetylation with dilute hydrochloric acid, gives with phenyl-hydrazine an over-all yield of 60 per cent. of d-glucosephenyl-osazone; (b) glucal triacetate is transformed by ozone in glacial acetic acid solution into the triacetyl derivatives of d-arabinose and an acid, which is probably arabonic acid; (c) the colour reaction with pine shavings; (d) the proof of the presence of only three hydroxyl groups in hydroglucal. These show that glucal contains the normal carbon chain present in dextrose, that the double bond

[48] T., 1919, 115, 300.
[49] Sitzungsber. K. Akad. Wiss. Berlin, 1913, 311; A., 1913, i, 445.
[50] E. Fischer, M. Bergmann, and H. Schotte, Ber., 1920, 53, [B], 509; A., i, 420.

is between the first and second carbon atoms, and that it is related to furan, whilst the presence of a butylene-oxide formation in hydroglucal is suggested by its stability towards hydrochloric acid, which renders an ethylene- or propylene-oxide structure most improbable.

The structural formula for sucrose which is now considered the most likely is that put forward by W. N. Haworth and Law in 1916, in which this sugar is represented as formed by the fusion of α-glucose having the butylene-oxide structure, and of α-fructose having the ethylene-oxide structure:

$$\text{OH·CH}_2\text{·CH(OH)·CH·[CH·OH]}_2\text{·CH·O·}\overset{\overset{\displaystyle \text{CH}_2\text{·OH}}{|}}{\text{C}}\text{—CH·[CH(OH)]}_2\text{·CH}_2\text{·OH.}$$
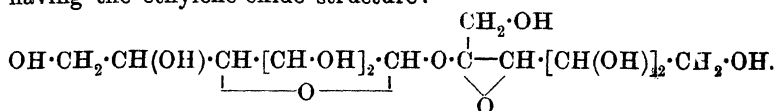
When sucrose is hydrolysed in the presence of acids, these forms are the first to be produced, but subsequently they rapidly undergo isomeric changes, giving successively the corresponding butylene-oxide form of fructose and then an equilibrium mixture of the α- and β-modifications of this, whilst alongside the β-butylene-oxide form of glucose with small amounts of the γ- or ethylene-oxide form of this sugar are produced. On these assumptions, the rotation and low crystallising power of invert-sugar are explained by the complexity of the mixture. Some evidence in favour of this is afforded [51] by contrasting the reducing powers of sucrose while undergoing inversion by (a) invertase and (b) dilute acid by measurements of the time taken to decolorise permanganate, but the formula given above is well substantiated by further investigation by Haworth [52] of the cleavage products of methylated sucrose. In previous investigations, the separation of the cleavage products of octamethyl sucrose was difficult, but heptamethyl sucrose is easily prepared, and, on hydrolysis with dilute hydrochloric acid, yields a trimethyl glucose and a tetramethyl fructose, which are readily separated by fractional distillation under a very low pressure. The trimethyl glucose was characterised by further methylation, which gave tetramethyl α-glucose. The tetramethyl fructose decolorised permanganate, behaved generally as a γ-sugar, and, when oxidised by nitric acid, gave an anhydro-acid or semi-lactide, the analysis of which agreed with an empirical formula, $C_{16}H_{30}O_{11}$. A closely reasoned argument shows that the properties of this point to its formation from an α-hydroxy-acid, which in turn could only be formed from the tetramethyl fructose having the formula

$$\text{OMe·CH}_2\text{·C(OH)·CH·CH(OMe)·CH(OMe)·CH}_2\text{·OMe.}$$
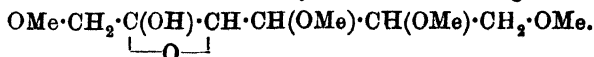
[51] E. F. Armstrong and T. P. Hilditch, *T.*, 1920, 117, 1086.   [52] *Ibid.*, 199.

The extensive study of the alkylated sugars, with which the names of Purdie, Irvine, and Haworth are mainly associated, has obviously opened out a general method for the determination of the constitution of the di- and poly-saccharides, for now that the properties and structures of a large number of alkylated aldoses and ketoses are known, the substances formed in the degradation of polysaccharides may be identified. The original method of alkylation by means of silver oxide and alkyl iodide is not always successful, owing to experimental difficulties, often caused by the insolubility of the carbohydrate in the alkyl iodide, but now that the alternative method of methylation is available in the use of methyl sulphate and sodium hydroxide rapid progress has been made. An investigation of the constitution of the polysaccharides by means of their hydrolysis must include the identification of (1) the constituent sugars, (2) their stereochemical form, (3) the hydroxyl groups involved in the coupling of the constituents, and (4) the position of the internal oxygen ring in each sugar. These methods have now been applied with considerable success to the elucidation of the structure of inulin,[53] and of the conversion of cellulose into glucose.[54]

Inulin, being soluble in aqueous sodium hydroxide, is readily methylated by methyl sulphate to dimethyl inulin, which has the advantageous property of being soluble in methyl iodide. Exhaustive methylation, however, by silver oxide and methyl iodide showed that the formation of trimethyl inulin represented the limit of the reaction. The hydrolysis of this at 100° with 1 per cent. oxalic acid proceeded quite smoothly, and yielded a trimethyl fructose, which, in view of its strong reducing properties, was undoubtedly a member of the γ-, that is, the supposed ethylene-oxide, series of ketoses. The trimethyl fructose was then converted into the corresponding trimethyl fructosides, which, on further methylation and subsequent hydrolysis, yielded the tetramethyl γ-fructose obtained by Haworth[55] from sucrose. The diagram on p. 67 illustrates the great advances made recently in our knowledge of the structural relationship of the four compounds.

The yields obtained in the conversion of inulin to trimethyl γ-fructose show that it is an aggregate of γ-fructose residues, each ketose molecule having lost two hydroxyl groups in the formation of the polysaccharide.

Further deductions from this research suggest* one of two alternative formulæ for inulin, which undoubtedly has a smaller

[53] J. C. Irvine and (Miss) E. S. Steele, *T.*, 1920, **117**, 1474.
[54] J. C. Irvine and C. W. Soutar, *ibid.*, 1489.
[55] *Loc. cit.*, see p. 65.

Inulin →	Fructose ←	Sucrose	→ Glucose
↓	↓	↓	↓
Dimethyl inulin	Tetra-acetyl fructose	Heptamethyl sucrose	Methyl-glucoside (α or β)
↓	↓	↓	↓
Trimethyl inulin	Tetra-acetyl methyl-fructoside	Trimethyl glucose →	Tetramethyl methyl-glucoside
↓	↓	and	↓
Trimethyl γ-fructose	Methyl-fructoside	Tetramethyl γ-fructose	Tetramethyl α-glucose
↓	↓		
Trimethyl γ-methyl-fructoside	Tetramethyl methyl-fructoside	↑	
↓	↓		
Tetramethyl γ-methyl-fructoside	Tetramethyl-fructose		

molecular weight than that given in the literature, and developments of the investigation will be looked for with great interest.

The conversion of cellulose into glucose has been studied by many workers, but not in a strictly quantitative manner, for as Irvine and Soutar point out, the evidence of specific rotation and reducing power, even when apparently consistent, cannot be held to characterise an uncrystallisable syrup as a definite sugar. Some advance has been made in a recent paper by K. Hess and W. Wittelsbach [56] on the acetolysis of ethyl cellulose, but in all work on the hydrolysis of cellulose where a yield of glucose even approximating to the theoretical amount has been claimed, in no case have the results been based on the quantity of a crystalline sugar or of a characteristic derivative actually isolated. The St. Andrews results now described have given, by the degradation of a purified cotton cellulose, a yield of crystalline derivatives of glucose equivalent to 85 per cent. of the theoretical amount. The method consisted in treatment of the cellulose with acetic anhydride and sulphuric acid, after which the soluble and insoluble products were converted into methylglucoside. The methylglucoside obtained was quite free from any isomeric methylhexoside, so that

[56] *Zeitsch. Elektrochem.*, 1920, **26**, 232 ; *A.*, i, 532.

mannose and galactose residues are not present in cellulose. The results point to the following formula for cellobiose,

$$OH \cdot CH \cdot [CH \cdot OH]_2 \cdot CH \cdot CH - O - CH \cdot [CH \cdot OH]_2 \cdot CH \cdot CH(OH) \cdot CH_2 \cdot OH$$
$$\underline{\quad O \quad} \quad \dot{C}H_2 \cdot OH \quad \underline{\quad O \quad}$$
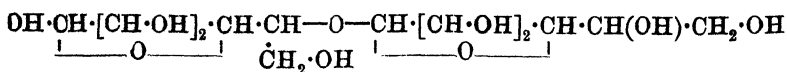
and afford some evidence of the structure of a portion of the cellulose molecule.

Nitrogen Compounds.

The catalytic formation of amines by the Sabatier process is usually unsatisfactory, owing to the difficulty of separating the mixture of primary and secondary amines generally formed. A. Mailhe[57] has, however, shown that the hydrogenation of ketazines in the presence of reduced nickel can be used for the preparation of primary amines if the reaction is carried out at specially low temperatures (about 130°), higher temperatures converting ketazines, and even the low temperatures aldazines,[58] into mixtures of primary and secondary amines. On the other hand, catalytic methods appear to be very convenient for the preparation of certain aliphatic and aromatic nitriles,[59] which are formed when vapours of the esters and ammonia are passed over aluminium or thorium oxide heated to 480—500°. The quantitative formation of hydrogen cyanide when carbon monoxide and ammonia are passed over thoria heated at 430° is a reaction which may become of considerable importance.

A very easy method of preparing guanidine is described by E. A. Werner and J. Bell,[60] who show that commercial dicyanodiamide is depolymerised at 120° in the presence of ammonium thiocyanate, giving an 80 per cent. yield of guanidine thiocyanate.

The α-methyl and α-ethyl derivatives of hydroxylamine[61] are obtained by the prolonged treatment of the corresponding disulphonic acids with concentrated sulphuric acid. The potassium salts of these acids, $RO \cdot N(SO_3K)_2$, are formed by the reactions between alkyl iodides and aqueous solutions of potassium hydroxylaminedisulphonate, and in general, like the potassium salts of the alkylimidosulphonates,[62] $NR(SO_3K)_2$, are noteworthy on account of their sparing solubility in water; thus potassium ethylene-

[57] *Compt. rend.*, 1920, **170**, 1265 ; *A.*, i, 475.   [58] *Ibid.*, 1120 ; *A.*, i, 475.
[59] *Ann. Chim.*, 1920, [ix], **13**, 226 ; *A.*, i, 476
[60] *T.*, 1920, **117**, 1133.
[61] W. Traube, H. Ohlendorf, and H. Zander, *Ber.*, 1920, **53**, [B], 1477 ; *A.*, i, 717.
[62] W. Traube and M. Wolff, *ibid.*, 1493 ; *A.*, i, 716.

diamine-NN'-tetrasulphonate dissolves only to the extent of 0·2 gram in 100 c.c. of water at the ordinary temperature, whilst the corresponding barium dipotassium is practically insoluble.

A convenient method [63] of preparing cyanogen chloride on a laboratory scale is the action of chlorine on a 12 per cent. solution of hydrogen cyanide. It has been shown that the reaction proceeds quantitatively according to the equation $Cl_2 + HCN = CNCl + HCl$. The pure substance does not undergo polymerisation, but in the absence of water hydrogen chloride causes the slow formation of cyanuric chloride.   ROBERT H. PICKARD.

<center>PART II.—HOMOCYCLIC DIVISION.</center>

<center>*Theoretical.*</center>

THE determination of the energy of atomic linkings in carbon compounds is intimately connected with that of the distribution of valency, and of all the available methods which can assist in throwing further light on these problems, it is probably the thermochemical that is most free from pitfalls in the domain of theory. Considerable progress has been made in the interpretation of the data supplied by the heats of combustion of hydrocarbons. Weinberg [1] points out that the heats of combustion of saturated hydrocarbons can be very nearly expressed by assuming that each carbon atom and each hydrogen atom contributes a constant quantity independent of the constitution. On this hypothesis, the heats of combustion of ethane and propane show that each carbon contributes 96·5 Cal. and each hydrogen 29·65 Cal. Again, from the known increment for each ·CH_2· and from the average heats of combustion of the octanes, the respective values 96 and 30 are obtained. The conclusion is drawn that the energies of rupture of C–H and C–C bonds do not materially differ, and although there seems to be a loophole in this part of the argument, interesting results follow from the application of the additive hypothesis to the case of the unsaturated hydrocarbons. The value calculated from the number of carbon and hydrogen atoms in the molecule subtracted from the observed heat of combustion gives a measure of the additional energy due to the unsaturated linkings. For a single ethylene bond, the increment thus obtained is about 30, or

[63] T. S. Price and S. J. Green, *J. Soc. Chem. Ind.*, 1920, 39, 98T ; *A.*, i, 425.
[1] A. von Weinberg, *Ber.*, 1919, 52, [B], 1501; *A.*, ii, 14.

15 for each unsaturated carbon atom. For the conjugated $\Delta^{\alpha\delta}$-hexadiene the increment is not 60, but only 16·3, and this is justifiably regarded as the increase due to the mutually restricted oscillation of three pairs of unsaturated atoms. If, then, the view of Thiele, that benzene contains three conjugated double bonds, is correct, we have to do with six pairs of unsaturated atoms, and the increment should be 32·6. Actually, it is 32·7 or 30·3, according as the value for the heat of combustion of benzene determined by Roth and Wallasch[2] or by Richards and Barry,[3] respectively, is accepted. It should be pointed out that the above argument might well be reversed, since most chemists will be ready to admit the cyclic conjugation of the benzene molecule, and if the latter is represented by the formula I, then it would seem that $\Delta^{\alpha\delta}$-hexadiene should be represented by the expression II. In

$$Me·C = CH$$
$$Me·C = CH$$

(I.) (II.)
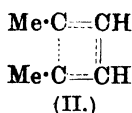
this way, the striking analogies between the properties of certain compounds containing conjugated double bonds and others of true aromatic type might receive some explanation. From the above, it will be seen that the energy of each carbon atom in benzene is about 5 Cal. above the normal for the carbon atom of a paraffin, whilst in ethylene the increment is 15 for each carbon atom. It is therefore particularly striking that in naphthalene and anthracene this increment per carbon atom is also about 5 Cal. Accordingly, all the carbon atoms in these polynuclear hydrocarbons are in a similar condition of unsaturation, and we are led to postulate complete cyclic conjugation in these cases also. The ortho-quinonoid formula for anthracene (III) which Auwers[4] deduces from his observations of the exaltation of the refractive and dispersive powers of 9-*iso*amylanthracene becomes IV if complete conjugation is assumed. There is nothing in the experiments which militates against this view, although a decisive argument is furnished against the adoption of the old idea of a central para-linking, since dihydroanthracenes behave optically exactly as if they contained two normal benzene nuclei.

(III.) (IV.)
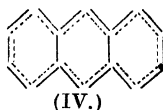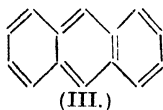
[2] *Annalen*, 1915, **407**, 134; *A.*, 1915, ii, 146.
[3] *J. Amer. Chem. Soc.*, 1915, **37**, 993; *A.*, 1915, ii, 421.
[4] K. von Auwers, *Ber.*, 1920, **53**, [B], 941; *A.*, i, 540.

Fajans[5] has developed a formula for the calculation of the heats of combustion and of formation of hydrocarbons from a more fundamentally sound point of view than that of Weinberg, but the chief interest of his work in relation to the present subject lies in the applications of his methods by Steiger[6] and by Hückel.[7] The former shows that the energy of the C–C linkings in graphite and in aromatic hydrocarbons is almost identical, and draws the conclusion that there is a close analogy in the arrangement of the carbon atoms and in the subdivision of their valencies in the molecules of all these substances. The latter has employed the considerations developed by Fajans and by Steiger to the determination of the energy of polymethylene rings, in order to compare the results with those which might be anticipated from Baeyer's theory. The value for $\cdot CH_2 \cdot$ in open chains is known to be 158 Cal., and the abnormal energy of polymethylenes can therefore be very simply estimated by dividing the heat of combustion by the number of carbon atoms, and comparing the value for the polymethylene $\cdot CH_2 \cdot$ thus obtained with the normal. In this manner, the values 170, 168·5, 165·5, 159, 158 are obtained for the methylene group in ethylene, cyclopropane, cyclobutane, cyclopentane, and cyclohexane respectively. These results are in general agreement with the strain theory, but the values obtained for even such simple derivatives as the methylpolymethylenes and also for cycloheptane require further elucidation.

Sidgwick[8] has passed in review the boiling points of a very large number of position-isomeric benzene derivatives, and has pointed out some hitherto unrecognised regularities and certain interesting exceptions. The derivatives of benzene may be roughly divided into two classes, the normal, in which the boiling points of isomeric ortho-, meta-, and para-compounds do not differ by much more than 10°, and the abnormal, in which the difference is more than 10°, and usually from 20—80°. In the normal series the substituents are of the unchangeable type, and may be alkyl (not aryl), alkyloxy-, or ester groups. In the abnormal series the boiling points of the meta- and para-derivatives are fairly close together, whilst the ortho- is much lower; the substituents here are of a reactive type, such as hydroxyl, carboxyl, amino-, and nitroxyl. These relations extend to the solubilities in water, so far as they have been observed. The isomerides in a normal series exhibit similar solubilities, whereas in abnormal compounds

[5] K. Fajans, *Ber.*, 1920, **53**, [B], 643; *A.*, ii, 354.
[6] A. L. von Steiger, *ibid.*, 666; *A.*, ii, 355.
[7] W. Hückel, *ibid.*, 1277; *A.*, i, 603.
[8] N. V. Sidgwick, *T.*, 1920, **117**, 389.

this is not the case; and where one of the substituents is hydroxyl, the unexpected result is noted that the ortho-derivative is far less readily soluble in water than the meta- or para-derivatives.

A good example of an abnormal series is that of the nitrophenols. o-Nitrophenol boils about 80° lower than the m- and p-nitrophenols, and it is also much less readily soluble in water. The chlorides of the phthalic acids are anomalous, having the boiling points: o-, 281°; m-, 276°; p-, 259°. If the explanation is that the ortho-derivative has a ring structure, as seems quite probable on chemical grounds, then this view should logically be extended to the meta-derivative also, and the work of von Braun (see below) removes much of the prejudice which might have been felt against such an assumption. In almost all cases a para-compound boils at a higher temperature than the isomeric meta-derivative, but in eleven series in which this rule is reversed one of the substituents is always amino- or substituted amino-. This indicates a constitutional peculiarity for which no explanation is as yet forthcoming.

Some interesting work has been carried out on the influence of nitro-groups on the reactivity of substituents in the benzene nucleus. Kenner and Parkin[9] studied the action of ammonia and of sodium methoxide on 2:3-, 3:4-, and 2:5-dinitrotoluenes, and explain their results in terms of a hypothesis which may be briefly stated in the following propositions: (a) Meta-directive groups activate substituents in the ortho- and para-positions, and ortho-para-directive groups have a similar effect on those in the meta-position. (b) The displacement of mobile substituents depends primarily on the formation of a molecular additive compound which undergoes rearrangement or decomposition leading to the reaction product. (c) The group responsible for the formation of the additive compound is not itself displaced. (d) Steric hindrance may be the orientating factor in a displacement by affecting the initial process of addition. This is a somewhat complex hypothesis, and it is unfortunate that it appears to be necessary to have recourse to that most unsatisfactory of expedients, steric hindrance, but the facts are certainly difficult to reconcile with a more simple explanation. In 2:3-dinitrotoluene, for example, it is the 2-nitroxyl which is displaced, and this is explained by assuming that steric hindrance prevents the 2-nitro-group from partaking in the formation of an additive product which occurs by the agency of the 3-nitro-group, and therefore the 2-nitro-group is displaced. With 3:4-dinitrotoluene, however, the activating influence of the ortho-para-direc-

[9] J. Kenner and M. Parkin, T., 1920, 117, 852.

tive methyl group is able in the absence of steric hindrance to be the deciding factor, and the nitroxyl in the 3-position is displaced. The experiments of Holleman and his collaborators [10] on the displacement of groups in the dichloronitrobenzenes and chlorodinitrobenzenes are examined from this point of view, and the results are, in the main, shown to be in good accord with the theory. During the present year the latter work has been extended [11] to the eleven dichlorodinitrobenzenes, and by means of a qualitative and quantitative study of the action of sodium methoxide on these isomerides several interesting points have been illustrated. The activity of a nitro-group, for example, is found to be strengthened by the introduction of a chlorine atom in the meta-position.

Kenner and Parkin give good reasons (*loc. cit.*) for rejecting the theory that the intermediate products postulated have a quinonoid structure, but there is at least one case, the displacement of nitroxyl by methoxyl in *s*-trinitrobenzene, in which the existence of a quinonoid intermediate stage is the simplest assumption which can be made to explain an otherwise anomalous reaction.

There are a number of cases in the literature of substances which may have a chain connecting the meta-positions in the benzene nucleus, but Braun and his collaborators have now prepared a series of substances which undoubtedly contain such ring systems and of a type which has hitherto been deemed incapable of existence. . ●The first example was a heterocyclic substance obtained by the reduction of julolidine methochloride,[12] and this was followed [13] by the observation that *m*-xylylene dicyanide on reduction by means of sodium and alcohol yields as the main product the saturated secondary amine (V) in which the C_2H_4-group may have the ethylene or ethylidene arrangement. The quaternary dimethylammonium hydroxide obtained from it in the usual manner loses water and dimethylamine on distillation, furnishing the unsaturated hydrocarbon (VI), which may be reduced

$-C_2H_4$
NH
$CH_2 \cdot CH_2$
(V.)

$-C_2H_4$
CH:CH
(VI.)

$-C_2H_4$
$CH_2 \cdot CH_2$
(VII.)
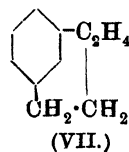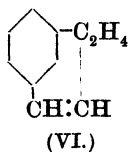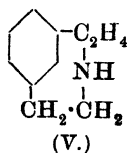
[10] *Rec. trav. chim.*, 1915, **35**, 1 ; *A.*, 1916, i, 22.

[11] A. F. Holleman and A. J. den Hollander, *ibid.*, 1920, **39**, 435; *A.*, i, 539.

[12] J. von Braun and L. Neumann, *Ber.*, 1919, **52**, [B], 2015; *A.*, i, 87.

[13] J. von Braun, (Frl.) L. Karpf, and W. von Garn, *ibid.*, 1920, **53**, [B], 98; *A.*, i, 251.

D*

by means of hydrogen in the presence of colloidal palladium to the saturated hydrocarbon (VII).

All three substances are converted by oxidation into *iso*phthalic acid. The two hydrocarbons have characteristic odours and abnormally low densities. This significant discovery is certain to stimulate numerous further investigations.

Statements at variance with the current stereochemical doctrine are prone to be regarded with suspicion, and perhaps more particularly when made in connexion with the chemistry of cinnamic acid and its isomerides, for in few branches of research has it been so frequently necessary to correct or reinterpret published experiments. It is now claimed [14] that on fusing cinnamic anhydride with tartaric acid, cinnamates are formed which "induce" optical activity in a portion of the cinnamic acid, so that optically active cinnamic acid may be extracted from the fusion by means of light petroleum. If the fact be as stated we may well accept the theory, but much more evidence is needed as to the homogeneity of the optically active material. An interesting asymmetric synthesis of a novel type is that of *l*-menthyl *d*-phenyl-*p*-tolylacetate, which is obtained by the interaction of *l*-menthol and phenyl-*p*-tolylketen in ethereal solution.[15] This represents one of the simplest and least unexceptionable examples of asymmetric synthesis which has been placed on record.

The two stereoisomeric forms of the enolic modification of ethyl phenylpyruvate, and also the ketonic modification, have now been prepared.[16] The solid enol (α: m. p. 51—52°) is that which was already known.[17] On distillation it is slowly changed into a more stable liquid enol (β), and this by the action of sodium acetate becomes the ketonic modification (γ: m. p. 79°).

$$\begin{array}{ccc}
\underset{\textstyle\alpha.}{\overset{\textstyle H\cdot C\cdot Ph}{\underset{\displaystyle HO\cdot C\cdot CO_2Et}{\big|\big|}}} &
\underset{\textstyle\beta.}{\overset{\textstyle Ph\cdot C\cdot H}{\underset{\displaystyle HO\cdot C\cdot CO_2Et}{\big|\big|}}} &
\underset{\textstyle\gamma.}{CH_2Ph\cdot CO\cdot CO_2Et}
\end{array}$$
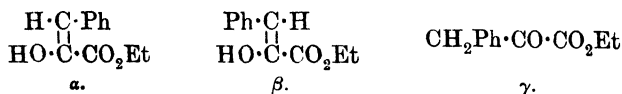
The α- and β-isomerides are readily brominated at $-15°$, and yield a dibromide which rapidly loses hydrogen bromide at the ordinary temperature with the formation of ethyl phenylbromopyruvate. The concordance between theory and practice is complete, especially since the γ-form can be brominated only in boiling carbon disulphide, and then yields a complex product.

[14] E. Erlenmeyer and G. Hilgendorff, *Biochem. Zeitsch.*, 1920, **103**, 79; *A.*, i, 615.

[15] R. Weiss, *Monatsh.*, 1919, **40**, 391; *A.*, i, 555.

[16] H. Gault and R. Weick, *Compt. rend.*, 1920, **171**, 395; *A.*, i, 675.

[17] J. Bougault, *ibid.*, 1914, **158**, 1424; *A.*, 1914, i, 839; J. Bougault and (Mlle) R. Hemmerlé, *ibid.*, 1915, **160**, 100; *A.*, 1915, i, 78.

There is very little real progress to record in connexion with the problem of the relation of colour to constitution, perhaps because the most active workers in this field are devoting their energies to the solution of those more fundamental difficulties which their earlier investigations disclosed. Among those who apply the organic chemist's instinct to this subject Kauffmann is prominent, and the development of his views will be followed with sympathetic interest. A communication [18] which is characteristic of the author's point of view contains an account of the theory of the colour of triphenylcarbinol salts based on the hypothesis of divisible valency, and also a description of experiments made to illustrate the point that basic function and colour-producing function of auxochromes do not run on parallel lines. The isomeric dimethoxybenzaldehydes (2:5-, 3:4, and 2:4-) were condensed with a series of substances containing a reactive methylene group such as nitromethane, phenylacetonitrile, and diketohydrindene, and in all cases it was found that the resorcinol derivative was most basic and least coloured, whilst the quinol derivative was least basic and most coloured and the catechol derivative occupied an intermediate position. It may be noted in passing that the colourless triamino-triphenylmethyl cyanide prepared from pararosaniline and potassium cyanide passes into a coloured dissociating cyanide under the influence of the light of an iron arc.[19]

Turning to the subject of reaction mechanism, it is certainly noteworthy, although not at all surprising, that certain unsaturated hydrocarbons containing conjugated ethylene linkings can combine with negatively substituted diazonium salts with the formation of normal azo-compounds.[20] Thus the compound

$$CH_2:CMe\cdot CMe:CH\cdot N_2\cdot C_6H_4\cdot NO_2$$
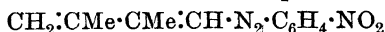
is readily obtained from dimethylbutadiene and p-nitrobenzene-diazonium chloride in glacial acetic acid solution. Curiously enough, it may be reduced by means of tin and hydrochloric acid to a corresponding aminohydrazo-derivative. The occurrence of this coupling reaction is held to support the view that diazo-salts react with aromatic compounds by virtue of an addition to a conjugated system of double bonds. This will be readily admitted, but, in view of the enormously greater readiness with which the reaction occurs in the case of phenols and amines, it seems reasonable to include the unsaturated oxygen or nitrogen atoms in the conjugated system. In this way, too, the theory of Karrer,[21] that

[18] H. Kauffmann, *Ber.*, 1919, **52**, [B], 1422; *A.*, i, 50.
[19] I. Lifschitz and C. L. Joffé, *ibid.*, 1919; *A.*, i, 95.
[20] K. H. Meyer and V. Schoeller, *ibid.*, 1468; *A.*, i, 97.
[21] *Ibid.*, 1915, **48**, 1398; *A.*, 1915, i, 1073.

addition occurs at the oxygen of phenols or their ethers and at the nitrogen of aromatic amines, is satisfactorily brought into line, and the numerous cases of hydrolysis of phenol ethers during coupling become explicable.

Various Reactions and Synthetical Methods.

Halogenation.—Chlorine may be introduced into the side-chain of toluene and certain derivatives by treating these substances with aqueous hypochlorous acid at temperatures below 0°.[22] It is possible to prepare in this manner benzyl chloride, benzylidene chloride, chlorobenzyl chloride (but not dichlorobenzyl chloride), xylyl chloride, and tolylidene chloride.

Aromatic nitro-compounds when heated with bromine to a high temperature in sealed tubes are changed in many cases to corresponding bromo-derivatives which often suffer further bromination. The reaction[23] is not a novel one, but has not been employed to any considerable extent as an instrument of research. Many fresh examples are recorded, and advantage is taken of the process to demonstrate that the crude nitration product of anthraquinone contains in all probability the 1 : 2- and 1 : 3-dinitroanthraquinones. Following up the clue, the 1 : 3-isomeride has actually been isolated from the reaction mixture.[24]

Sulphonation.—Iodine is a powerful catalyst in sulphonation, and, for example, it is claimed that an excellent yield of *o*-sulphobenzoic acid is obtained from benzoic acid.[25] The catalyst has, therefore, a definite orientating effect.*

Quinol[26] reacts with aqueous sodium hydrogen sulphite at 100° with the formation of sodium *cyclo*hexane-1 : 4-diol-1 : 2 : 4-trisulphonate, whilst resorcinol[27] under the same conditions is changed to a substance which appears to be the sodium bisulphite compound of *cyclo*hexane-3 : 5-dionesulphonic acid.

Nitration.—The intensely coloured by-product obtained in the nitration of thymol ethyl ether was first isolated by Kehrmann

[22] Levinstein, Ltd., H. Levinstein, and W. Bader, *Brit. Pat.* 134250; *A.,* i, 21.

[23] S. N. Dhar, *T.,* 1920, 117, 993.   [24] *Ibid.,* 1001.

[25] J. N. Rây and M. L. Dey, *ibid.,* 1405.

* Mr. J. Ogilvie, who has repeated the experiment of the sulphonation of benzoic acid under the conditions prescribed in this paper, reports that he is able to confirm the catalytic effect of iodine in the reaction. On alkali-fusion of the product, however, *m*-hydroxybenzoic acid (m. p. 199—200°) was produced, and there was no evidence of the formation of salicylic acid.

[26] W. Fuchs and B. Elsner, *Ber.,* 1919, 52, [B], 2281; *A.,* i, 159.

[27] *Ibid.,* 1920, 53, [B], 886; *A.,* i, 545.

and Messinger,[28] and later studied by Decker and Solonina,[29] who regarded the substance as a quinonoid anhydro-salt of dicymyl-hydroxylamine N-oxide. The discovery that in many cases the perchlorates of these bases can be readily isolated has led to more extended investigations [30] embracing the action of nitric acid on other phenol ethers. The nitration product of anisole, added to perchloric acid, gives a crystalline precipitate of the perchlorate (VIII), and this may be reduced to di-p-anisylamine, or by very gentle treatment to di-p-anisylnitric oxide (IX).

$$OMe \cdot C_6H_4 \cdot N(:O):C_6H_4:O<^{Me}_{ClO_4} \qquad NO(C_6H_4 \cdot OMe)_2$$
$$\text{(VIII.)} \qquad\qquad\qquad \text{(IX.)}$$
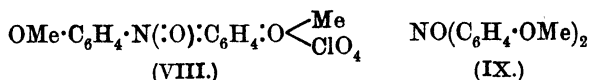
The quinonoid perchlorate yields solutions which are pure blue in thin layers and red in deep layers. The nitric oxide has the appearance of copper powder, and is much more stable than the corresponding diphenyl derivative,[31] and this is remarkable, since di-p-tolylnitric oxide is less stable than the latter substance.

Replacements.—The direct conversion of bromobenzene into benzoic acid, p-dibromobenzene into terephthalic acid, p-bromo-aniline into p-aminobenzoic acid, and similar transformations in the benzene, naphthalene, and thiophen series, may be accomplished by the action of aqueous or aqueous alcoholic potassium cyanide in the presence of cuprous cyanide at 200°.[32] Although copper is the unique catalyst in this reaction, and also in the displacement of halogen directly attached to the nucleus by hydroxyl or amino-groups, other elements or their compounds may be of practical service in effecting the transformations of diazonium compounds. Thus the double cyanide of nickel and potassium may be used for the preparation of nitriles by the Sandmeyer method with good results,[33] and cobalt thiocyanate is an excellent catalyst for the conversion of diazonium salts into the corresponding thiocyanates. Nickel and cobalt salts are, however, ineffective in the preparation of halogen derivatives through the diazonium salts.

Aromatic acids may in certain cases be reduced to aldehydes via their anilides and related phenyliminochlorides. These are converted by stannous chloride in ethereal solution into the tin double

[28] *Ber.*, 1901, **34**, 1626; *A.*, 1901, i, 484; compare F. Kehrmann, *Ber.*, 1919, **52**, [B], 2119; *A.*, i, 156.

[29] *Ibid.*, 1902, **35**, 3217; *A.*, 1902, i, 767.

[30] K. H. Meyer and H. Gottlieb-Billroth, *ibid.*, 1919, **52**, [B], 1476; *A.*, i, 37.

[31] H. Wieland and M. Offenbächer, *ibid.*, 1914, **47**, 2111; *A.*, 1914, i, 955.

[32] K. W. Rosenmund and E. Struck, *ibid.*, 1919, **52**, [B], 1749; *A.*, i, 44.

[33] A. Korczyński, W. Mrozinski, and W. Vielau, *Compt. rend.*, 1920, **171**, 182; *A.*, i, 643.

salts of Schiff's bases, which may be hydrolysed, and good yields of the aldehydes are so obtained.[34]   Benzaldehyde, cinnamaldehyde, *p*-hydroxybenzaldehyde (starting from *p*-ethylcarbonatobenzoic acid), and 3 : 4 : 5-trimethoxybenzaldehyde have been prepared in this way.

Friedel-Crafts Reaction.—The action of cyanogen bromide on various aromatic substances in the presence of aluminium chloride has been further investigated[35] and good results have been obtained, especially with the phenol ethers, which are converted into nitriles. The method will be serviceable in those cases where the corresponding hydroxy-acid is not conveniently prepared by the usual methods, such as the Kolbe synthesis and the action of bicarbonates on the polyhydric phenols. Cyanogen chloride gives the same products as the bromide, and is almost equally reactive.

A modification of the Friedel-Crafts reaction has been described,[36] and consists essentially in the employment of an aromatic hydrocarbon with aluminium powder and excess of mercuric chloride. It is thought that the reaction proceeds in accordance with the equation

$$C_6H_6 + Al + 2HgCl_2 = C_6H_5AlCl_3 \cdot HgCl + Hg,$$
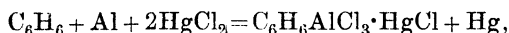
and the large excess of mercuric chloride is designed to avoid the production of mercury. Using this product as catalyst, a number of remarkable results have been obtained. For example, thianthren is prepared from benzene and sulphur in a yield of 85 per cent. of that theoretically possible.

Closely associated with the Friedel-Crafts reaction in performance, although not in theory, is Hoesch's synthesis, which, it will be recalled, is based on the production of the ketimine hydrochlorides by the condensation of nitriles with phenols by hydrogen chloride in the presence of anhydrous zinc chloride and ether. Hydroxy- and methoxy-acetonitriles have now been employed in this reaction, and condensed with such phenols as resorcinol and its methyl ether and phloroglucinol. In some cases, the use of zinc chloride is found to be unnecessary, and a 94 per cent. yield of ω-methoxyresacetophenone is obtained by hydrolysing the initial product of the condensation of methoxyacetonitrile and resorcinol in ethereal solution by means of hydrogen chloride.[37]

Formaldehyde Condensations.—The usual assumption is that the condensation of formaldehyde with aniline and its derivatives, with

[34] A. Sonn and Ernst Müller, *Ber.*, 1919, **52**, [B], 1927; *A.*, i, 58.

[35] P. Karrer, A. Rebmann, and E. Zeiler, *Helv. Chim. Acta*, 1920, **3**, 261; *A.*, i, 389.   [36] J. N. Rây, *T.*, 1920, **117**, 1335.

[37] W. K. Slater and H. Stephen, *ibid.*, 309.

the formation of substituted diphenylmethanes, occurs exclusively in the para-position with respect to the amino-group. This is erroneous, and the product from dianilinomethane or from anhydroformaldehydeaniline and aniline is a mixture of $4:4'$- and $2:4'$-diaminodiphenylmethanes in the proportions of approximately nine to one.[38] Examination of 'the nitro-derivatives of the crude product supplied the first clue, and methods were later evolved for the actual separation of the constituents of the mixture. The production of $2:4'$-diaminodiphenylmethane (X) in this condensation is paralleled by that of diaminophenylacridine (XI) in the magenta fusion.
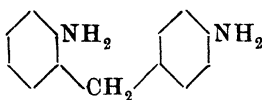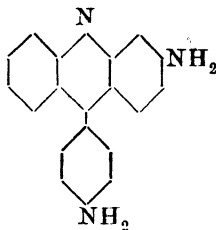
(X.)   (XI.)

A careful study of the conditions of condensation of chloromethyl ether and dichloromethyl ether with aromatic compounds has led to the elaboration of a novel method for the direct introduction of the chloromethyl group into the aromatic nucleus.[39]

Of the various suggested processes, that which depends on the condensation of the aromatic hydrocarbons with s-dichloromethyl ether in the presence of zinc chloride appears to be the most satisfactory in practice. It is unnecessary to employ highly purified dichlorodimethyl ether, the crude oil from the action of hydrogen chloride on 40 per cent. aqueous formaldehyde being utilisable, and it is even an advantage in some examples to employ the whole crude product without separation of the aqueous layer, and in that case sufficient anhydrous zinc chloride is added ultimately to form $ZnCl_2,2H_2O$. Benzyl chloride, p-xylylene dichloride, p-chlorobenzyl chloride, and other similar substances were successfully prepared, and the reaction is also applicable to the introduction of the bromomethyl group.

The condensation of styrene with formaldehyde yields β-phenyltrimethylene glycol (XII) and its methylene ether. Anethole gives rise to a similar product, whilst camphene in glacial acetic acid solution is changed by trioxymethylene into homocamphenol

[38] H. King, *T.*, 1920, **117**, 988.
[39] H. Stephen, W. H. Short, and G. Gladding, *ibid.*, 510.

acetate.[40] Homocamphenol or camphenylidene-6-ethanol has been oxidised to the corresponding aldehyde and acid, and numerous derivatives have been prepared.

$$CHPh(CH_2 \cdot OH)_2 \qquad CHPh\!:\!CH \cdot CH\!:\!CH \cdot CO \cdot NH_2$$
$$\text{(XII.)} \qquad\qquad \text{(XIII.)}$$

$$CHPh\!:\!CH \cdot CH\!:\!CH \cdot NH \cdot CO_2Me \qquad CHPh\!:\!CH \cdot CH_2 \cdot CHO$$
$$\text{(XIV.)} \qquad\qquad \text{(XV.)}$$
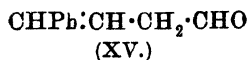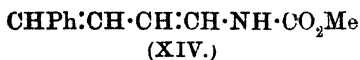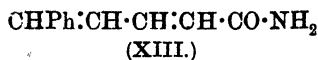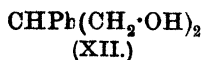
Hofmann Reaction.—It is well known that the Hofmann reaction for the preparation of amines from acid amides does not proceed smoothly with $\alpha\beta$-unsaturated amides, but this is due to the ready hydrolysis of the unsaturated amines into an aldehyde and ammonia. Experimental details have now been recorded[41] applicable to the control of this process, and enabling the final product to be isolated. To take an example, cinnamenylacrylamide (XIII) is treated with sodium hypochlorite in the presence of methyl alcohol, and the product is cinnamenylvinylurethane (XIV), which is hydrolysed by sulphuric acid to β-benzylidene-propaldehyde (XV). If the process is a reasonably general one, it will have many applications.

Oxidation.—The catalytic oxidation of benzene by gases containing oxygen at temperatures of 300—700° results in the production of p-benzoquinone and maleic acid.[42] The process is clearly of technical interest, and a large variety of catalysts are claimed, but probably none is so effective as the first-named, which is vanadium oxide distributed on pumice.

It is perhaps worth noting, in view of the ever-increasing application of the method of ozonisation, that potassium ferrocyanide reduces many ozonides of unsaturated substances with the minimum formation of tarry by-products.[43] The constitution of a number of enols has been probed by examining the products of their oxidation by ozone.[44]

The anodic oxidation of benzoic acid introduces hydroxyl groups into the nucleus.[45] Catechol, quinol, 2:5-dihydroxybenzoic acid, and a hydroxyquinolcarboxylic acid were isolated from the product.

The oxidation of amines still engages attention, and Gold-

[40] H. J. Prins, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, 22, 51; *A.*, i, 42; G. Langlois, *Ann. Chim.*, 1919, [ix], 12, 265; *A.*, i, 241.

[41] I. J. Rinkes, *Rec. trav. chim.*, 1920, 39, 200; *A.*, i, 322.

[42] J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, 1920, 12, 228; *A.*, i, 426.

[43] C. Harries, *D.R.-P.* 321567; *A.*, i, 675.

[44] J. Scheiber and G. Hopfer, *Ber.*, 1920, 53, [B], 697, 898; *A.*, i, 487, 552.

[45] F. Fichter and E. Uhl, *Helv. Chim. Acta*, 1920, 3, 22; *A.*, i, 234.

schmidt [46] finds that Bamberger's hypothesis, that phenylhydroxyl-amine is the sole first stage in the oxidation of aniline, is inadequate, since that substance is not sufficiently reactive to explain the formation of the polynuclear oxidation products. An additional first stage is therefore postulated in the bivalent radicle PhN:, which polymerises into azobenzene, benzoquinonephenyldi-imine, $NPh:C_6H_4:NH$, and emeraldine.

By carrying out the oxidation of amines with a free para-position in ether by means of lead peroxide and anhydrous sodium sulphate, azo-compounds and quinonearyldi-imines are produced, and, what is still more interesting, the oxidation of a mixture of amines yields mixed azo-compounds and mixed quinonearyldi-imines. Triphenylhydrazine is oxidised at $-60°$ in methyl ether to hexaphenyltetrazane, $NPh_2 \cdot NPh \cdot NPh \cdot NPh_2$, which can be isolated as a green crust, and forms solutions in ether, which are pale greenish-blue at $-80°$, and deep blue at the ordinary temperature. This is probably due to dissociation into the radicle, triphenylhydrazyl, $NPh_2 \cdot NPh \cdots$, relatively stable to oxygen, but easily combining with nitric oxide. Wieland and his school have continued the study of the ditertiary hydrazines, [47] but the results, although of great interest, are along the lines of previous work emanating from the same laboratory. Tetrabenzylhydrazine shows no tendency to dissociate, and it appears that this phenomenon is conditioned by the direct attachment of the nitrogen to the nucleus, and that it is intensified when there are ortho-para-directive substituents in the ring.

Unsaturation.

Pinene, nopinene, and γ-pinene have remarkable avidity for hydrogen chloride and hydrogen bromide, so that, especially at elevated temperatures, these hydrocarbons will actually decompose aniline hydrochloride and ammonium chloride, with the formation of the hydrochlorides of the terpenes. Bornyl chloride is also formed by double decomposition between pinene and numerous chlorine-containing terpene derivatives, such as sylvestrene dihydrochloride and camphene hydrochloride. [48] The observation may be of practical, as well as of theoretical, interest, since it would be difficult to devise a more neutral reagent than a terpene, and this is frequently a desideratum in processes which involve the removal of the elements of halogen acids.

[46] S. Goldschmidt, *Ber.*, 1920, **53**, [B], 28; *A.*, i, 226, 258.
[47] H. Wieland and E. Schamberg, *ibid.*, 1329; *A.*, i, 768.
[48] O. Aschan, *Öfvers. Finska Vet.-Soc.*, 1916, **58**; *A.*, i, 316:

The possible number of polymerides of an unsymmetrical ethylene derivative of the form aCH:CHb is very great, even when the dimerides alone are calculated and the constitution is restricted to the possible *cyclo*-butanes and butylenes. Theory indicates two *cyclo*butanes, each existing in four stereoisomeric modifications, and five butylenes, each of which would have *cis*- and *trans*-forms. That is, there are eighteen possibilities, without including the enantiomorphous or racemic modifications. Puxeddu[49] restricts the possible number of polymerides of anethole to eleven, and has now succeeded in isolating the seventh known substance of this type by fractionally distilling in a vacuum, and afterwards crystallising the white precipitate obtained by the addition of ferric chloride to an ethereal solution of the anisylmethylethylene.

At 120—180°, two molecules of isoprene rapidly attack one of p-benzoquinone, with the production of a substance, to which the formula XVI has been provisionally assigned.[50] It forms a tetrabromide and dioxime. The reaction is clearly related to the

(XVI.)   (XVII.)
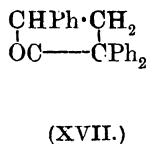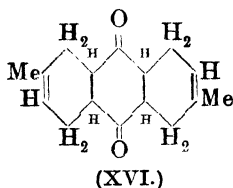
polymerisation of isoprene itself, with the formation of dimethyl-*cyclo*octadiene.

A further numerous class of similar reactions are those which involve the formation of *cyclo*butane derivatives from the ketens. Dimerisation of the latter produces *cyclo*butanediones, whereas with ethylene derivatives the addition of ketens yields *cyclo*butanones.[51] Thus styrene condenses with diphenylketen, with production of the compound XVII, and many other examples have been recorded. *cyclo*Pentadiene reacts with one molecule of diphenylketen, whilst N-methylpyrrole reacts with two molecules, even when the components are applied in molar proportions. Attempts have been made to prepare the optically active camphorketen, in order to facilitate by polarimetric methods the study of these additive reactions, but only partial success was achieved. The most successful experiments were those on the action of quinoline on camphorcarboxyl chloride. The resulting solution contains the desired product in the free state for a short period,

[49] E. Puxeddu, *Gazzetta*, 1920, **50**, i, 149; *A.*, i, 481.
[50] H. von Euler and K. O. Josephson, *Ber.*, 1920, **53**, [B], 822; *A.*, i, 489.
[51] H. Staudinger and E. Suter, *ibid.*, 1092; *A.*, i, 556.

but it is very reactive, and quickly passes over into its dimerides. The fact that these were isolated in stereoisomeric modifications is opposed to Schroeter's view that these substances are molecular compounds bound together loosely by partial valencies, and is strong evidence that they are correctly regarded as normal *cyclo*butane derivatives.[52]

· Some extremely suggestive results have been obtained in the course of an investigation of the behaviour of diphenylnitric oxide towards other radicles, such as nitric oxide and triphenylmethyl.[53] Diphenylnitric oxide, $Ph_2N\!:\!O$, is apparently the analogue of nitrogen peroxide, and when treated with nitric oxide at 0°, the initial product is probably $O\!:\!NPh_2\!\cdot\!N\!:\!O$, which is the analogue of nitrogen trioxide. The products actually isolated are the nitroso-derivatives of diphenylamine and *p*-nitrodiphenylamine, and the mechanism of their production is probably as follows. The hypothetical intermediate isomerises into diphenylnitroamine, $Ph_2N\cdot NO_2$, and then nitrodiphenylamine, $NO_2\cdot C_6H_4\cdot NHPh$, which when produced is immediately nitrosated by the supposed intermediate, in accordance with the scheme:

$NO_2\cdot C_6H_4\cdot NHPh + O\!:\!NPh_2\cdot N\!:\!O = NO_2\cdot C_6H_4\cdot NPh\cdot NO + NPh_2\cdot OH$.
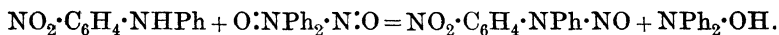
Auto-decomposition of diphenylhydroxylamine produces diphenylamine, which is itself nitrosated according to a similar scheme. That an analogue of nitrogen trioxide is actually produced in this reaction may be proved by performing the process in the presence of a secondary base, such as di-*p*-tolylamine, when large amounts of the related nitrosoamine can be isolated. With triphenylmethyl, diphenylnitric oxide yields the compound XVIII, the initial product being so unsaturated that it unites with a second molecule of the hydrocarbon. The constitution of the substance follows from the products obtained by catalytic hydrogenation. These are diphenylamine and *p*-benzhydryltetraphenylmethane, the nature of which has been elucidated by Tschitschibabin.[54]

$$Ph_2N\cdot O\cdot CPh_2\!\!\diagup\!\!\overline{}\!\!\diagdown\!\!CPh_3.$$

(XVIII.)
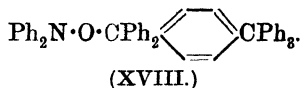
Molecular Rearrangement.

The smooth transformation of *n*-butylaniline into 4-butylaniline by heating with hydrochloric acid or certain metallic chlorides[55]

[52] H. Staudinger and S. Schotz, *Ber.*, 1920, **53**, [B], 1105; *A.*, i, 557.

[53] H. Wieland and K. Roth, *ibid.*, 210; *A.*, i, 304.

[54] *Ibid.*, 1904, **37**, 4709; *A.*, 1905, i, 125.

[55] J. Reilly and W. J. Hickinbottom, *T.*, 1920, **117**, 103.

is of interest, on account of the fact that no rearrangement of the butyl radicle occurs in the process.   It will be recalled that Ladenburg found that propylpyridinium salts gave α-*iso*propylpyridine on heating, and there are many similar instances.   The statement in the theoretical discussion of the process that the reaction cannot be satisfactorily explained by assuming the intermediate formation of butyl chloride is of doubtful validity, and experimental evidence opposed to the theory of double decomposition and re-synthesis is not put forward.

Attempts during the present year [56] to generalise the Claisen transformation have been quite unsuccessful, and the rearrangement of phenolic ethers into substituted phenols on heating appears to be characteristic of the allyl ethers.

β-Naphthyl vinyl ether, which does not undergo the transformation, has an intense odour of tangarine skins.[57]

A pinacone–pinacoline type transformation, which involves the conversion of a hydrogenated naphthalene into a hydrindene derivative, is illustrated in the annexed scheme, the reagent employed being silver nitrate in ethereal solution.[58]
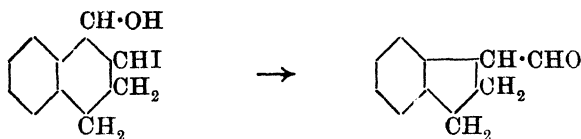
When benzophenoneoxime is warmed with phosphorus pentasulphide, it yields thiobenzanilide as the result of a Beckmann change.   It is now found that the rearrangement is due to the formation of an ester of the thio-oxime, since, if the reaction is carried out in ethereal suspension, thiobenzophenoneoxime hydrogen phosphate, $HO \cdot PO(SN:CPh_2)_2$, is obtained, and this changes into thiobenzanilide at 70° with almost explosive violence.[59]

Still another transformation has been discovered which is conditioned by, and peculiar to, the allyl group.   Methylallylaniline *N*-oxide, $CH_2:CH \cdot CH_2 \cdot O \cdot NPhMe:O$, heated in presence of alkali in a current of steam, is converted into *N*-phenylmethyl-*O*-allyl-hydroxylamine, $CH_2:CH \cdot CH_2 \cdot O \cdot NMePh$.[60]

[56] S. G. Powell and R. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 646; *A.*, i, 381.

[57] J. von Braun and G. Kirschbaum, *Ber.*, 1920, **53**, [B], 1399; *A.*, i, 728.

[58] M. Tiffeneau and A. Orékhoff, *Compt. rend.*, 1920, **170**, 465; *A.*, i, 313.

[59] M. Kuhara and K. Kashima, *Mem. Coll. Sci. Kyoto*, 1919, **4**, 69; *A.*, i, 314.

[60] J. Meisenheimer, *Ber.*, 1919, **52**, [B], 1667; *A.*, i, 35.

Natural Products.

Chlorogenic acid, the tannin-like constituent of coffee, has been re-examined,[61] and found to have a relatively simple constitution. It is apparently a depside of caffeic acid and quinic acid, in which the carboxyl group of the caffeic acid assumes the ester function, as shown in the formula:

$$C_6H_3(OH)_2 \cdot CH \colon CH \cdot CO \cdot O \cdot C_6H_7(OH)_3 \cdot CO_2H.$$
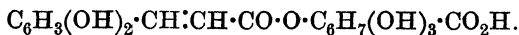
Aspidinol and an isomeric compound, ψ-aspidinol, are obtained by condensation of butyronitrile with methylphloroglucinol β-monomethyl ether in the presence of hydrogen chloride.[62] The two compounds are doubtless the 3- and the 5-butyryl derivatives of the methylphloroglucinol methyl ether, but it is not yet possible to assign one formula or the other to aspidinol. In connexion with the synthesis of plant pigments and other natural products containing the phloroglucinol nucleus, it should be noted that phloroacetophenone, $C_6H_2(OH)_3 \cdot COMe$, can be obtained by the hydrolysis of the pyranol, which is the isolated product of the Nencki condensation applied to phloroglucinol.[63]

The investigation of capsaicin has been continued, and the pungent principle has been regenerated from synthetical vanillyl-amine[64] and decenoyl chloride from the decenoic acid obtained by hydrolysis of capsaicin.[65] There is little remaining doubt that the substance is decenylvanillylamide. As regards the constitution of the acid fragment, a little progress has been possible, since the fusion of this decenoic acid with potassium hydroxide furnishes acetic acid and an octoic acid with a branched chain. This proves that the α-carbon atom is joined only to the carboxyl group and one other carbon atom, but it gives no information relating to the position of the double bond, because it is well known that oleic acid and many of its isomerides yield acetic and palmitic acids on fusion with alkali hydroxides.

The colouring matter of henna leaves, lawsone, has the empirical formula $C_{10}H_6O_3$, and from its chemical behaviour the conclusion is drawn that it is a hydroxynaphthaquinone, and probably identical with 2-hydroxy-1 : 4-naphthaquinone.[66]

The attack on the problem of carminic acid has been resumed,

[61] K. Freudenberg, *Ber.*, 1920, **53**, [B], 232 ; *A.*, i, 322.
[62] P. Karrer and F. Widmer, *Helv. Chim. Acta*, 1920, **3**, 392 ; *A.*, i, 441.
[63] K. B. Sen and P. C. Ghosh, *T.*, 1920, **117**, 61.
[64] E. K. Nelson, *U.S. Pat.* 1329272 ; *A.*, i, 543.
[65] E. K. Nelson, *J. Amer. Chem. Soc.*, 1920, **42**, 597 ; *A.*, i, 380.
[66] G. Tommasi, *Gazzetta*, 1920, **50**, i, 263 ; *A.*, i, 626.

and, largely from analogy to the more closely investigated kermesic acid and the similar behaviour of carminic acid towards reducing and oxidising agents, the. formula XIX has been assigned to the substance.[67] Carminic acid is optically active, and the side-chain of unknown constitution is doubtless of sugar-like character; nevertheless, the substance is certainly not a glucoside. It yields an octa-acetyl derivative, and by careful treatment a hexa-acetyl derivative, which may be oxidised by lead tetra-acetate to an unstable diquinone reducible by sulphurous acid. The moderated acetylation of carminic acid therefore leaves two hydroxyl groups in the α-position in the anthraquinone nucleus unaffected.

(XIX.)
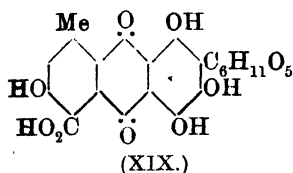
Simonsen [68] has isolated a new dicyclic terpene from the constituents of Indian turpentine from *Pinus longifolia*, Roxb. It has a characteristic, sweet odour, and forms a crystalline nitrosate. On treatment with hydrogen chloride in ethereal solution, it yielded a mixture of d-sylvestrene and dipentene hydrochlorides, and this conversion into the meta- and para-series at once suggested the possibility that the hydrocarbon is a carene having one of the formulæ

(*A*) Δ^3-Carene. (*B*) Δ^4-Carene. (*C*) Dehydrocarane.
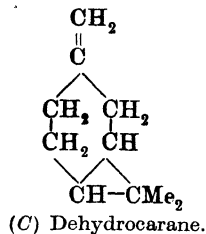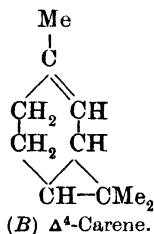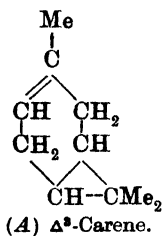
On oxidation by means of potassium permanganate, dimethylmalonic acid, and, under other conditions, *trans*-caronic acid, were obtained, so that this view was amply confirmed. The molecular refraction was found to be 44·22, which is in good agreement with the calculated value (44·19) for a compound containing a *cyclo*hexane and a *cyclo*propane ring, and which does not contain conjugated linkings or other causes of optical abnormality. This in

[67] O. Dimroth and H. Kammerer, *Ber.*, 1920, **53**, [B], 471; *A.*, i, 442.
[68] J. L. Simonsen, *T.*, 1920, **117**, 570.

itself favours the formula A, and is almost decisive against B. C is improbable, since the glycol obtained by very careful permanganate oxidation does not react with phthalic anhydride in benzene solution, an indication that the group ·CH$_2$·OH is absent. The terpene is dextrorotatory, and is called d-carene. It is very probably d-Δ^3-carene, and is the first naturally occurring terpene which has been found to contain the carane ring.

Alicyclic Group.

When it is considered how difficult it may be to introduce two alkyl groups into certain esters, for example, ethyl benzoylacetate, which form relatively stable sodium derivatives, it appears remarkable that the alkylation of 2-methyl*cyclo*hexanone by means of methyl or ethyl iodides and sodamide should give rise to 2:2-dimethyl*cyclo*hexanone or the corresponding methylethyl derivative respectively.[69] The dialkylated ketones condense with benzaldehyde to form benzylidene derivatives, so that there is no doubt as to the correctness of the constitutions assigned. Considerable improvements have been effected in the technique of the catalytic reduction of aromatic amines,[70] and the conditions can now be regulated so as to obtain either a *cyclo*hexylamine or a di*cyclo*hexylamine as the main product. The catalyst employed is colloidal platinum, of which a rather larger proportion than usual is necessary. Thus, in reducing a monoamine, a catalyst concentration of about 0·6 per cent. is employed, and for a diamine about twice as much. The influence of temperature, concentration, and proportion of hydrochloric acid present in the mixture are all marked. Excellent yields of *cyclo*hexylamine or di*cyclo*hexylamine are obtained from aniline, and the reduction of the toluidines and m- and p-nitroanilines has been effected with equally good results. The methyl*cyclo*hexylamines from the three toluidines are each obtained in stereoisomeric forms, recognised by the production of α- and β-benzoyl derivatives. The new availability of these useful bases will probably provide a further stimulus to the study of partly hydrogenated aromatic hydrocarbons, which are readily obtained from them by applying the process of exhaustive methylation.

A communication of quite outstanding interest is that of Beesley and Thorpe,[71] dealing with the preparation of derivatives of

[69] A. Haller and R. Cornubert, *Compt. rend.*, 1920, **170**, 700, 973; *A.*, i, 390, 441.

[70] A. Skita and W. Berendt, *Ber.*, 1919, **52**, [B], 1519; *A.*, i, 27.

[71] R. M. Beesley and J. F. Thorpe, *T.*, 1920, **117**, 591.

*dicyclo*butane and *tricyclo*butane. A new system of nomenclature of associated alicyclic systems is proposed, and this is capable of accurately expressing in words and symbols the constitutions of the most complex interlocked structures. It is simple and logical, but a shortened exposition would serve no useful purpose, and the original must be consulted. In view of the fact that the introduction of the new nomenclature is a recent event, the compounds mentioned below are described in the ordinary way, the numbering of the *dicyclo*butane ring commencing at the tertiary carbon atom. ββ-Dimethylpropanetricarboxylic acid (XX) is converted into the dibromo-ester (XXI), and the latter is found to be changed by concentrated aqueous potassium hydroxide at a high temperature into 1-methyl*dicyclo*butane-2:3:4-tricarboxylic acid (XXII).

$$
\begin{array}{ccc}
\mathrm{CMe} \!\!<\!\! \begin{array}{l} \mathrm{CH_2 \cdot CO_2H} \\ \mathrm{CH_2 \cdot CO_2H} \\ \mathrm{CH_2 \cdot CO_2H} \end{array}
&
\mathrm{CMe} \!\!<\!\! \begin{array}{l} \mathrm{CHBr \cdot CO_2Et} \\ \mathrm{CHBr \cdot CO_2Et} \\ \mathrm{CH_2 \cdot CO_2Et} \end{array}
&
\mathrm{CMe} \!\!<\!\! \begin{array}{l} \mathrm{CH \cdot CO_2H} \\ \mathrm{C \cdot CO_2H} \\ \mathrm{CH \cdot CO_2H} \end{array}
\\
\text{(XX.)} & \text{(XXI.)} & \text{(XXII.)}
\end{array}
$$
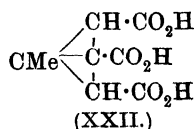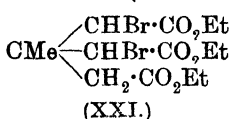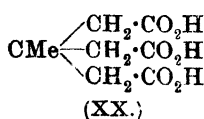
This remarkable compound can theoretically exist in three stereoisomeric modifications, and, in point of fact, three modifications have been isolated, melting at 154°, 193°, and 165° respectively. The first-mentioned readily yields an anhydride, the third does so with greater difficulty, whilst the second shows no tendency whatever to form an anhydride. The carboxyl group in position 3 is found on the models to point away from the system, and, moreover, methyl*tricyclo*butanetricarboxylic acid (see below) shows no tendency to form an anhydride, so that this property in the above acids is restricted to the carboxyl groups in positions 2 and 4. On this basis, the three isomerides have the configurations assigned in the following figures:
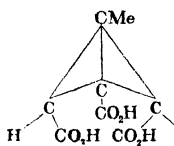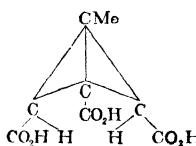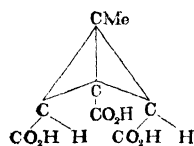
(M. p. 154°.)   (M. p. 193°.)   (M. p. 165°.)

The three acids are formed in approximately equal amount in the original reaction, and are separated by taking advantage of the fact that the acids are insoluble in ether, whilst the two anhydrides are readily soluble in this solvent. The mixture is therefore heated, and the anhydro-acid derived from the *meso-cis*-isomeride (m. p. 154°) extracted. The residue is treated with

acetic anhydride, when the racemic modification (m. p. 165°) is dehydrated, and can be similarly removed, leaving a residue of the *meso-trans*-acid (m. p. 193°). The neatest possible confirmation of the correctness of the assignment of the above formulæ is obtained by studying the behaviour of the three isomerides on bromination. The bromo-triethyl ester from the acid melting at 154° simply yields a stable bromo-acid when hydrolysed, and this harmonises with the configuration, because the bromine atom does not approach the groups in the molecule, with which it can react. The bromo-triethyl ester from the acid melting at 165° yields, on boiling with pyridine, a lactonic ester (XXIII), because in this case the bromine atom is close to a carboxyethyl group. When the acid melting at 193° is treated with phosphorus pentabromide and bromine, and the product poured into alcohol, a bromo-derivative is not formed at all, or, if formed, is too unstable to exist, and by loss of hydrogen bromide passes into an ester of methyl-*tricyclo*butanetricarboxylic acid (XXIV). This, again, accords well with the configuration assigned to the acid melting at 193°.

(XXIII.)   (XXIV.)
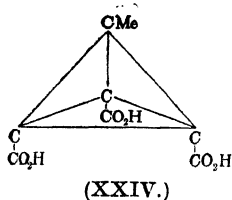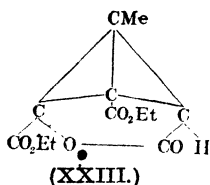
The acid, XXIV, the preparation of which was briefly announced in 1913,[72] may also be obtained in small yield by the action of hot aqueous potassium hydroxide on the tribromo-ethyl ester derived from $\beta\beta$-dimethylpropanetricarboxylic acid (XX). From the structural point of view it is one of the most interesting substances synthesised in recent years, for the tetrahedral arrangement of the four substituents is concentric with that of the four groups attached to a methane carbon atom. The symmetry of methane is reproduced exactly, and enantiomorphism should be possible in this series only when all four groups are different. Again, the tetrahedral unit, C_4, has the arrangement of atoms which is characteristic of the diamond crystal. It is most unfortunate that a group of substances in which so many crucial tests of the soundness of deductions from the models can be applied should be so difficult to prepare in large quantities.

The condensation of ethyl $\alpha\alpha'$-dibromo-$\beta\beta'$-dimethylglutarate with ethyl malonate in presence of alcoholic sodium ethoxide leads

[72] J. F. Thorpe, *P.*, 1913, **29**, 346.

to the formation of a yellow sodium salt, to which the constitution XXV was assigned.[73]   On hydrolysis by acids, the monobasic acid XXVI is ultimately obtained, and all the experimental evidence is in agreement with this view of the bicyclic nature of the substances.   It is now found that the acid XXVI is produced by the action of boiling dilute alkali hydroxides on $a\delta$-diketo-$\beta\beta$-dimethyl-hexoic acid (XXVII), which is obtained[74] on oxidising dehydro-*iso*fenchoic acid by means of potassium permanganate under special conditions.   Too much attention need not be paid to the conclusion drawn from this experiment that the formulæ XXV and XXVI are insufficiently grounded, and that the substances are, in reality, *cyclo*pentene derivatives, because the real existence of the fused *cyclo*propane ring has since been demonstrated in a convincing manner.[75]

$$CMe_2 \begin{array}{l} C(CO_2Et) \cdot C:C(ONa) \cdot OEt \\ C(CO_2Et) \cdot CO \end{array}$$

(XXV.)

$$\begin{array}{ccc} Me_2C & \!\!\!\!\!\!\!\!\!\!\! & C \cdot CO_2H \\ | & \diagup & CH_2 \\ HC & \!\!\!\!\!\!\!\!\!\!\! & CO \end{array}$$

(XXVI.)

$$CO_2H \cdot CO \cdot CMe_2 \cdot CH_2 \cdot COMe$$
(XXVII)
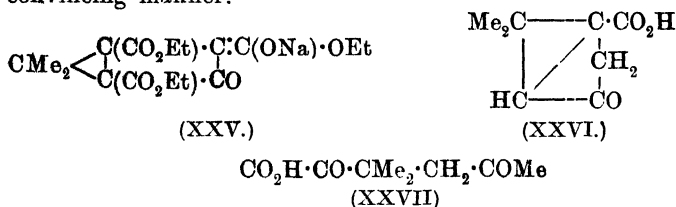
It is pointed out that the valencies in the *dicyclo*pentane system, especially the central connecting linking, are from theoretical considerations in a state of considerable strain, and far more so than in the *cyclo*propane ring of carone.   Thus, although carone may be readily oxidised by potassium permanganate, with the formation of *trans*-caronic acid, it by no means follows that, under the influence of the same reagent, the *cyclo*propane ring in the substances under discussion ought to be expected to behave in a similar fashion and to remain intact.   As a matter of fact, this is not the case, and the ring is broken by potassium permanganate, with the formation of open-chain acids.   When, however, the acid XXVIII, which is the initial product of the hydrolysis of XXV, is oxidised by means of potassium ferricyanide and potassium carbonate, it gives rise to *trans*-caronic acid.   The formation of

$$CMe_2 \begin{array}{l} CO \cdot CO_2H \\ CH_2 \cdot CO \cdot CH_3 \end{array} \rightarrow CMe_2 \begin{array}{l} C(OH)(CO_2H) \cdot CH_2 \\ CH_2 \!\!-\!\!\!\!- CO \end{array}$$

$$\downarrow$$

$$CMe_2 \begin{array}{l} C(CO_2H) \cdot CH_2 \\ CH \!\!-\!\!\!\!- CO \end{array} .$$
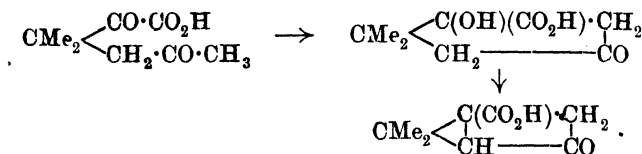
[73] W. H. Perkin, J. F. Thorpe, and C. Walker, *T.*, 1901, **79**, 729.
[74] N. J. Toivonen, *Annalen*, 1919, **419**, 176 ; *A.*, i, 49.
[75] E. H. Farmer and C. K. Ingold, *T.*, 1920, **117**, 1362.

XXVI from XXVII is therefore to be explained according to the above scheme (p. 90), the necessity for which is instructive. There is an obvious alternative scheme, in which the *cyclo*propane ring would be the first to be formed.

On account of its formulation by some chemists as an intermediate stage in the Wagner transformation, the hydrocarbon tricyclene (XXIX) has a special interest, and it has now been prepared [76] by a series of processes from tricyclenic acid (XXX), the constitution of which is not disputed.

$$CMe_2 \Big\langle {C(CO_2H) \cdot CH \cdot CO_2H \atop CH \text{------} CO}$$

$$H_2C\text{---}CH\text{---}CH_2$$
$$CMe_2$$
$$HC\text{------}CH$$
$$C \cdot CH_3$$

$$H_2C\text{---}CH\text{---}CH_2$$
$$CMe_2$$
$$HC\text{------}CH$$
$$C \cdot CO_2H$$

(XXVIII.)   (XXIX.)   (XXX.)
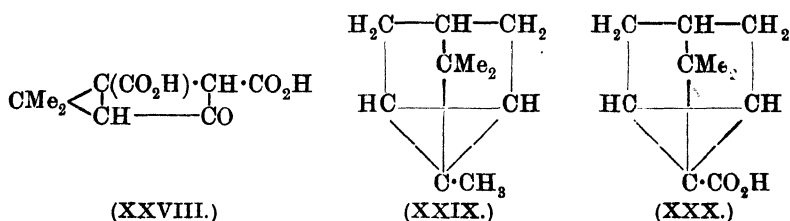
The methyl tricyclenate is reduced by sodium and alcohol to the corresponding primary alcohol, which is oxidised to an aldehyde, the hydrazone of which yields the desired hydrocarbon on heating at 180—195° with an alcoholic solution of sodium ethoxide. Tricyclene (m. p. 64—65°) is a relatively stable substance, which may be oxidised by potassium permanganate in acetic acid solution, with the formation of tricyclenic acid as one of the products, thus showing that the above process has not disturbed the ring system. It is converted by heating with sodium hydrogen sulphate into camphene, but the same change cannot be effected by means of zinc chloride in boiling benzene. The hydrocarbon might therefore be intermediate in the transformation of borneol, but not of *iso*borneol, into camphene. All arguments of this type are open to the objection that the abnormal energy conditions at the moment of reaction are not sufficiently taken into account.

Homocamphor (XXXI) has been prepared [77] by ring closure of hydrocamphorylacetic acid (XXXII), itself prepared by distillation of the malonic acid derivative produced in the electrolytic reduction of the condensation product of camphoric anhydride and diethyl sodiomalonate.

$$CH_2\text{---}CH\text{------}CH_2$$
$$CMe_2 \quad CH_2$$
$$CH_2\text{---}CMe\text{---}CO$$

$$CH_2\text{---}CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$$
$$CMe_2$$
$$CH_2\text{---}CMe \cdot CO_2H$$

(XXXI.)   (XXXII.)
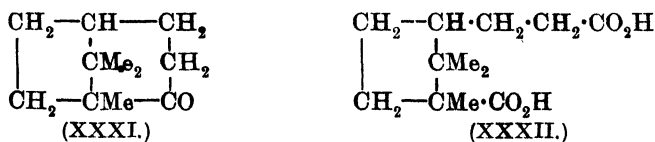
[76] P. Lipp, *Ber.*, 1920, **53**, [B], **769**; *A.*, i, 491.
[77] A. Lapworth and F. A. Royle, *T.*, 1920, **117**, 743.

The new substance is very like camphor in chemical and physical properties, and yields a similar series of derivatives. Its *iso*nitroso-derivative undergoes the Beckmann change, with the formation of a substance which yields homocamphoric acid on hydrolysis. This confirms the constitutions assigned to hydrocamphorylacetic acid and homocamphor.

Polycyclic Aromatic Groups.

Hydrindene Group —Ethyl $\beta\beta$-diphenyl-lactate, in contradistinction from the acid itself, dissolves in concentrated sulphuric acid to a green solution, from which 3-phenylindone (XXXIII) and two isomeric diphenyltruxones can be isolated [78] The diphenyltruxones are colourless dimerides of the orange-red phenylindone, and it is interesting to note that only one of them can be reduced to a tetrahydro-derivative, probably containing two ·CH·OH

(XXXIII.)   (XXXIV.)
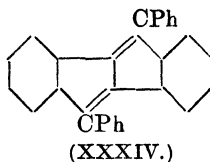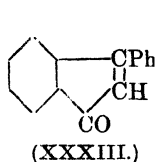
groups, by means of hydrogen in the presence of palladium. The brown hydrocarbon, which is prepared by the dehydration of the product of the action of magnesium phenyl bromide on diphensuccindandione (9:12), can be oxidised by chromic acid in cold acetic acid solution, with formation of 2:2′-dibenzoylbenzil, $C_6H_4Bz\cdot CO\cdot CO\cdot C_6H_4Bz$, and has therefore the constitution XXXIV.[79]

A series of similar substances has been prepared and investigated.

Naphthalene Group.—Chlorinated nitronaphthalenes not readily obtained in other ways may be prepared by the nitration of the naphthalene chlorides followed by removal of the elements of hydrogen chloride. Thus naphthalene tetrachloride and nitric acid yield a resinous nitro-derivative, which is transformed by weak alkaline reagents into 5:8-dichloro-1-nitronaphthalene.[80]   An extended study[81] of the reduction of α-naphthylamine shows that, in the presence of a neutral solvent, sodium and ethyl, butyl or amyl alcohols lead to the production of 5:8-dihydro-1-naphthylamine. This is also the product when ethyl or butyl alcohol is

[78] Remo de Fazi, *Gazzetta*, 1919, **49**, ii, 253; *A.*, i, 316.
[79] K. Brand and H. Ludwig, *Ber.*, 1920, **53**, [B], 809; *A.*, i, 486.
[80] O. Matter, *D.R.-P.* 317755; *A.*, i, 429.
[81] F. M. Rowe, *J. Soc. Chem. Ind.*, 1920, **39**, 241; *A.*, i, 609.

employed alone, but with amyl alcohol the reaction proceeds further, and *ar*-tetrahydro-α-naphthylamine is obtained. The explanation is that only under suitable conditions of temperature and alkyloxide concentration does the above-mentioned dihydro-derivative undergo isomerisation to 7 : 8-dihydro-1-naphthylamine, and that this isomerisation is an essential preliminary of reduction to the tetrahydro-stage. Similar results were obtained with naphthalene itself, which is first reduced to 1 : 4-dihydronaphthalene, isomerised to 1 : 2-dihydronaphthalene, and only then further reduced to tetrahydronaphthalene. In the catalytic reduction of naphthalene and α-naphthylamine dissolved in various solvents and in presence of nickel, it was found that the reduction almost always stopped at the first stage mentioned above.

Anthracene Group.—Phenols may be condensed with phthalic anhydride and its substitution products in the presence of aluminium chloride, and good yields are obtained when the solvent is *s*-tetrachloroethane.[82] The carboxybenzoyl group is introduced in the ortho-position to the phenolic hydroxyl, and in many cases the benzoylbenzoic acids formed can be smoothly dehydrated to anthraquinones. For example, 4-chloro-1-hydroxyanthraquinone can be prepared in this way from phthalic anhydride and *p*-chlorophenol.[82] In the section (see above) in which brief mention is made of the work of Dimroth on carminic acid, it was noted that two of the hydroxyl groups can be acetylated only with difficulty. This is a general property of hydroxyl groups in the α-positions in the anthraquinone nucleus. 1-Hydroxyanthraquinone is scarcely attacked under the conditions which suffice to complete the acetylation of the 2-derivative, and purpurin and alizarin-bordeaux can be readily changed to mono-2-acetates.[84]

When the hydrochloride of 1-aminoanthraquinone is exhaustively chlorinated in acetic acid solution, it yields the compound XXXV, which may be reduced by stannous chloride in acetic acid to 2 : 4-dichloro-1-hydroxyanthraquinone, or by ammonium chloride in acetic acid to 2 : 3 : 4-trichloro-1-hydroxyanthraquinone. The pentachloro-derivative is hydrolysed by warm sulphuric acid to tetrachlorohydroxybenzoylbenzoic acid (XXXVI), and at a higher temperature to phthalic acid and 2 : 3 : 4 : 5-tetrachlorophenol.[85]

Methyleneanthraquinone (XXXVII), a stable, pale yellow, crystal-

[82] F. Ullmann and W. Schmidt, *Ber.*, 1919, 52, [B], 2098; *A.*, i, 53.

[83] F. Ullmann and A. Conzetti, *ibid.*, 1920, 53, [B], 826; *A.*, i, 488.

[84] O. Dimroth, O. Friedemann, and H. Kammerer, *ibid.*, 481; *A.*, i, 443.

[85] K. Fries and E. Auffenberg, *ibid.*, 23; *A.*, i, 236.

line substance, is obtained by the condensation of a cold alkaline solution of anthranol with an excess of formaldehyde.[86]

$$C_6H_4 \begin{matrix} CO \cdot C \cdot CO - CCl_2 \\ CO \cdot C \cdot CCl_2 \cdot CHCl \end{matrix}$$

$$CO_2H \cdot C_6H_4 \cdot CO \underset{Cl}{\overset{OH}{\bigcirc}} \overset{Cl}{\underset{Cl}{\bigcirc}} Cl$$

(XXXV.)   (XXXVI.)

$$C_6H_4 \begin{matrix} -CO- \\ C(:CH_2) \end{matrix} C_6H_4$$

(XXXVII.)
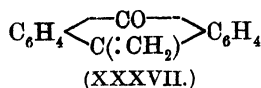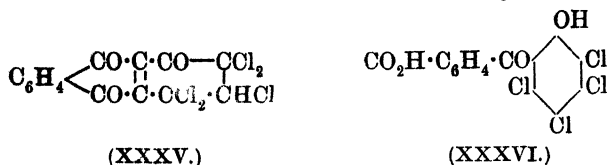
Polynuclear Groups.—Benzanthrone and most of its derivatives which have been examined in this connexion readily yield crystalline oxonium salts.[87] The ferrichlorides may be isolated from an acetic acid solution containing ferric chloride, but the salts do not separate in the presence of excess of hydrochloric acid. Indeed, it is necessary to avoid the addition of the latter acid, sufficient of which for the formation of the double salt is derived from the hydrolysis of a portion of the ferric chloride. A dihydroxybenzanthrone obtained by condensation of deoxyalizarin and glycerol in the presence of sulphuric acid is found to be readily methylated, and is regarded as having the constitution XXXVIII. Since the substance, which is termed " benzalizarin," has dyeing properties on mordants which closely resemble those of alizarin itself, it becomes clear that the propinquity of the two hydroxyl groups of the latter substance to the carbonyl of the quinone nucleus is not so important a factor as has been imagined, and *p*-quinonoid formulæ are suggested for the lakes of alizarin and benzalizarin.

$$\underset{(XXXVIII.)}{\overset{\text{OH}}{\underset{\text{CO}}{\text{HO}}}}$$

(XXXVIII.)
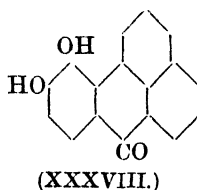
Perylene may be conveniently obtained in good yield by heating $2:2'$-dihydroxy-$1:1'$-dinaphthyl at 400—500° with a halogen compound of phosphorus and phosphorous acid.[88] This hydrocarbon is $1:8$-dinaphthylene, and the reaction is evidently ·one involving rearrangement, but this is not surprising under the conditions.

[86] K. H. Meyer, *Annalen*, 1920, **420**, 134; *A.*, i, 747.
[87] A. G. Perkin, *T.*, 1920, **117**, 696.
[88] F. Hansgirg and A. Zinke, *Monatsh.*, 1919, **40**, 403; *A.*, i, 541.

Compounds containing Boron, Phosphorus, and Metals.

A communication on boranilide has appeared[89] which is crowded with astonishing statements, but it is necessary to point out that the experiments as described hardly bear the construction which is put on them, and the analytical data supplied are quite inadequate to support even the views on the composition of the substances which have been prepared.

The action of aliphatic diazo-compounds on tertiary phosphines leads to the production of a new class of phosphorus derivatives termed phosphazines. The reaction is an additive one proceeding in accordance with the scheme:

$$CR_2\!:\!N\!:\!N + PR_3 \longrightarrow R_2C\!:\!N\!\cdot\!N\!:\!PR_3.$$
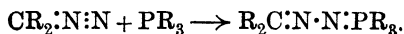
The products are basic, although this property is less developed when arylphosphines are the starting points. Triphenylphosphine-benzophenoneazine, $PPh_3\!:\!N\!\cdot\!N\!:\!CPh_2$, is obtained from triphenylphosphine and diphenyldiazomethane. It is slowly hydrolysed to benzophenonehydrazone and triphenylphosphine oxide. On being heated in a vacuum it loses nitrogen, and is converted into triphenylphosphinediphenylmethylene, $PPh_3\!:\!CPh_2$, which crystallises in red leaflets. When azides are added to phosphines the phosphazines which may be assumed to be formed initially decompose spontaneously, with the production of still another new type—the phosphineimines. Thus phenylazoimide and triphenylphosphine yield triphenylphosphinephenylimine, $PPh_3\!:\!NPh$, when mixed in dry ether. This imine reacts with diphenylketen in benzene solution in accordance with the scheme:

$$PPh_3\!:\!NPh + CPh_2\!:\!CO = \begin{matrix} PPh_3\!\cdot\!NPh \\ | \qquad | \\ O\!\!-\!\!-\!\!-\!C\!:\!CPh_2 \end{matrix} \longrightarrow O\!:\!PPh_3 \text{ and } NPh\!:\!C\!:\!CPh_2$$
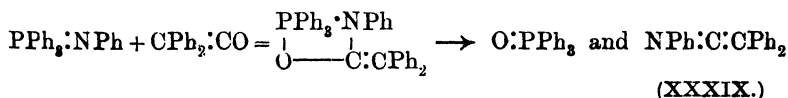
<div align="right">(XXXIX.)</div>

The compound, XXXIX, is the first member of the series of the keten-imines.[90] An enormous number of aromatic arsenic derivatives have been prepared and described,[91] but few new methods have been elaborated. The introduction of mercury in aromatic compounds is another subject that has been much investigated, and it appears to be possible to effect substitutions by

[89] T. C. Chaudhuri, *T.*, 1920, **117**, 1081.

[90] H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635; *A.*, i, 106; *Ber.*, 1920, **53**, [B], 72; *A.*, i, 228.

[91] R. G. Fargher, *T.*, 1920, **117**, 865; W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1919, **41**, 1587, 1600, 1610, 1809, 1822, 1826, 1834; *A.*, i, 107—117; compare *Brit. Pat.* 128181.

means of mercuric acetate in substances which are not affected by reagents that might be regarded as much more powerful. Phenol ethers react even with aqueous mercuric acetate to yield additive compounds, which are instantly transformed by sodium chloride into products mercurated in the nucleus. At 50° p-tolyl methyl ether gives the substance $3C_6H_4Me\cdot OMe\cdot Hg(C_2H_3O_2)_2,2HgO$, and by subsequent treatment with sodium chloride the substance

$$C_6H_3Me\cdot OMe\cdot HgCl.[92]$$
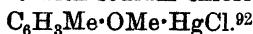
Mercuration differs from most substitution processes in that there is very little regularity, and each case has to be separately investigated. Lead tri-p-2-xylyl has been prepared [93] by the action of lead dichloride on the calculated amount of magnesium p-2-xylyl bromide, and this crystalline substance exhibits analogy to triphenylmethyl in its behaviour. It is bimolecular in benzene, and its solutions are coloured. At $-40°$ it combines with bromine in pyridine to yield lead tri-p-2-xylyl bromide, whilst in chloroform at $-10°$ the product is lead di-p-2-xylyl dibromide. Alkyl derivatives of bivalent tin have not yet been isolated in a pure condition, but the aryl derivatives, as usual, have proved more amenable and exhibit interesting properties.[94] Tin diphenyl is obtained by the addition of finely powdered stannous chloride to an ethereal solution of magnesium phenyl bromide. It is bright yellow, and gives yellow solutions. When freshly prepared it has the normal molecular weight, but five fold polymerisation soon occurs in benzene solution. R. ROBINSON.

PART III.—HETEROCYCLIC DIVISION.

THE work now to be reviewed has not equalled that of pre-war years in volume, but the progress achieved in various directions, notably in connexion with the alkaloids, has been such as to merit a fairly detailed account. At the same time, one or two investigations, which have extended over some years, appear to have reached a point at which they may conveniently be dealt with as a whole. For these reasons, this Report will probably be found to be not much shorter than those which have preceded it.

Some Aspects of the Addition Theory of Reactions.

Although the addition theory of reactions is very widely accepted, there is probably divergence of opinion as to whether, for instance, the equation:

[92] W. Manchot and F. Bössenecker, *Annalen*, 1920, **421**, 331; *A.*, i, 780.
[93] E. Krause and M. Schmitz, *Ber.*, 1919, **52**, [B], 2165; *A.*, i, 197.
[94] E. Krause and R. Becker, *ibid.*, 1920, **53**, [B], 173; *A.*, i, 340.

$$\begin{array}{cc} \underset{Y \cdot C}{X \cdot C} + \underset{B}{\underset{|}{A}} & \underset{X \cdot C \cdot B}{X \cdot C \cdot A} \\ (I.) \end{array} \qquad \begin{array}{cc} \underset{Y \cdot C \cdots B}{X \cdot C \cdots A} & \underset{Y \cdot C \cdots}{X \cdot C \cdots A - B \cdots} \\ (II.) \end{array}$$
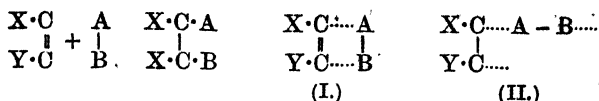
is an adequate expression of the process of saturation of a double bond. Thus Kekulé supposed that the final product was preceded by the double molecule (I), whilst more recently it has been assumed—and the view seems intrinsically more probable—that a still earlier stage is represented by (II). From this point of view much interest attaches to the direct formation of a cyclic structure by an additive reaction. With the exception of certain reactions of the ketens, all instances of this kind hitherto known depend on the union of similar molecules to form polymerides. Although these products are doubtless better represented by formulæ with ordinary rather than subsidiary linkages,[1] it seems more rational to consider them as the outcome, not of an instantaneous change, but of a continuous series of gradual changes, the phases of which are represented by (II) and (I). In the writer's view such a conception also supplies a simple explanation of the frequency with which four- rather than six-membered rings are produced in such cases. From the kinetic point of view, a reaction between two molecules is much more likely to occur than one between three, and similarly, unless other factors of an adverse kind operate, saturation of a preliminary product of the type (II) is more likely to occur by intramolecular rearrangement to type (I) than by intermolecular reaction with another molecule resulting in the formation of a six-membered ring. In illustration of this, a four-membered heterocyclic ring (IV) is produced with guaiacol when o-methoxyphenyl benzylidenehydrazinocarboxylate (III) is heated [2]:

$$CHPh{:}N{\cdot}NH{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}OMe \longrightarrow$$
(III.)

$$OH{\cdot}C_6H_4{\cdot}OMe + CHPh{:}N{\cdot}N{\cdot}CO \longrightarrow CHPh{:}N{\cdot}N{<}{\overset{CO}{\underset{CO}{}}}{>}N{\cdot}N{:}CHPh$$
(IV.)

$$H_2N{\cdot}N{<}{\overset{CO{\cdot}NH}{\underset{CO{\cdot}NH}{}}} \longleftarrow CHPh{:}N{\cdot}N{<}{\overset{CO{\cdot}NH}{\underset{CO{\cdot}NH}{}}}$$
(VI.)   (V.)

$$CHPh{:}N{\cdot}N{<}{\overset{CO}{\underset{CO}{}}}{>}N{\cdot}NH_2$$
(VII.)
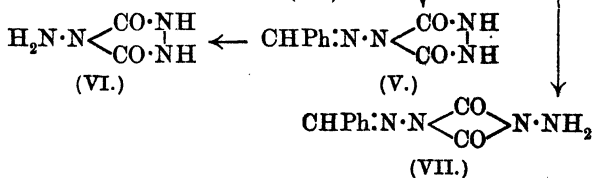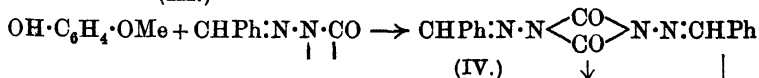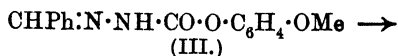
Although a trimeric formula supplies an equally good explanation of the successive formation of benzylideneurazine (V) and of

[1] H. Staudinger, Ber., 1920, 53, [B], 1073; A., i, 517.

[2] O. Diels and H. Grube, ibid., 854; A., i, 505; compare also the polymerisation of protoanemonin to anemonin, p. 114.

uracine itself (VI) on heating the compound with hydrochloric acid, the production of a compound corresponding in composition with the formula (VII) is only explicable on the basis of the dimeric formula.

That cyclic structures may also result from the combination of dissimilar molecules is evidenced by the formation of the acid chloride (I) with the corresponding anhydride (II) by the addition of phosphorus trichloride to phenyl styryl ketone in the presence of acetic anhydride [3]:

$$\begin{matrix} CPh\text{:}O \\ CH\text{:}CHPh \end{matrix} \rightarrow \left[\begin{matrix} CPh\text{——}O \\ CH\cdot CHPh \end{matrix} \hspace{-2mm}>\hspace{-1mm}PCl_3 \right] \rightarrow$$

$$\begin{matrix} CPh\text{——}O \\ CH\cdot CHPh \end{matrix}\hspace{-2mm}>\hspace{-1mm}POCl \rightarrow \left(\begin{matrix} CPh\text{——}O \\ CH\cdot CHPh \end{matrix}\hspace{-2mm}>\hspace{-1mm}PO \right)_2 .$$

$$\qquad\qquad (\text{I.}) \qquad\qquad\qquad\qquad (\text{II.})$$
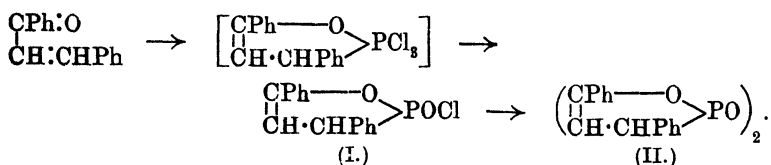
The reaction is the first in which it has been found that two valencies of the same atom are utilised to satisfy the unsaturation of a second molecule. Perhaps still more remarkably, it has been shown [4] that the products of the action of phosphorus trichloride on aldehydes, which are decomposed by water to form hydroxyphosphonic acids,[5] are to be represented by formulæ of the type (III). In this case also a mixture of an acid chloride (IV) and an anhydride (V) is produced in the presence of acetic anhydride, those from benzaldehyde being represented by the formulæ (IV) and (V):

$$\begin{matrix} CHPh\cdot O \\ \diagdown\ \diagup \\ PCl_3 \end{matrix} \rightarrow \begin{matrix} CHPh\cdot O \\ \diagdown\ \diagup \\ POCl \end{matrix} \rightarrow \left[\begin{matrix} CHPh\cdot O \\ \diagdown\ \diagup \\ PO \end{matrix} \right]_2 O \rightarrow$$

$$(\text{III.}) \qquad\qquad (\text{IV.}) \qquad\qquad (\text{V.})$$

$$\begin{matrix} CHPh\cdot O \\ \diagdown\ \diagup \\ PO\cdot OH \end{matrix} \rightarrow \begin{matrix} CHPh\cdot OH \\ | \\ PO(OH)_2 \end{matrix}$$

$$\qquad (\text{VI.}) \qquad\qquad (\text{VII.})$$
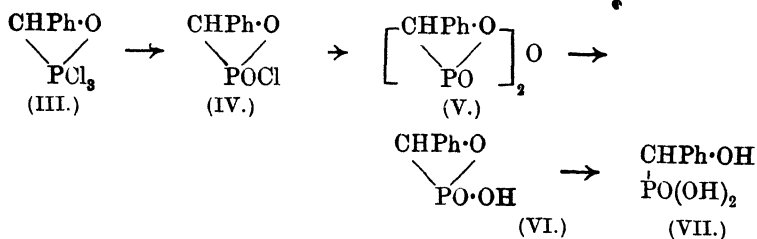
An unexpected point of difference between the two series of compounds is that in this case the free monobasic acid (VI) is sufficiently stable to be isolated. It reduces potassium permanganate slowly, whereas the hydroxyphosphonic acid (VII) suffers immediate oxidation.

In yet another instance, the formation of a cyclic structure has

[3] J. B. Conant and A. A. Cook, J. Amer. Chem. Soc., 1920, •42, 830; A., i, 454.

[4] J. B. Conant and A. D. Macdonald, ibid., 2337; A., 1921, i, 69.

[5] W. Fossek, Monatsh., 1884, 5, 120. 627; 1886, 7, 121; A., 1884, 833; 1885, 504; 1886, 529.

been presumed. Thus, a mixture of two stereoisomeric forms of ethyl $\alpha\beta$-dinitrocinnamate is produced by the action of nitrogen peroxide on ethyl phenylpropiolate, but the first product of their interaction in light petroleum solution is a labile, crystalline compound of the two in equimolecular proportions.[6] This product decomposes into its components if the attempt be made to isolate it in the ordinary way, but, on the other hand, it gradually passes over in a closed vessel into ethyl phenylpropiolate and ethyl dinitrocinnamate. The reactions are expressed as follows:

$$2CPh\text{:}C\cdot CO_2Et + 2NO_2 \longrightarrow
\begin{array}{c}
CPh\text{≡}C\cdot CO_2Et \\
\vdots \qquad \vdots \\
NO_2 \quad NO_2 \\
\vdots \qquad \vdots \\
CPh\text{≡}C\cdot CO_2Et
\end{array}
\longrightarrow
\begin{array}{c}
CPh\text{≡}C\cdot CO_2Et \\
| \qquad | \\
NO_2 \quad NO_2 \\
+ \\
CPh\text{:}C\cdot CO_2Et
\end{array} ,$$
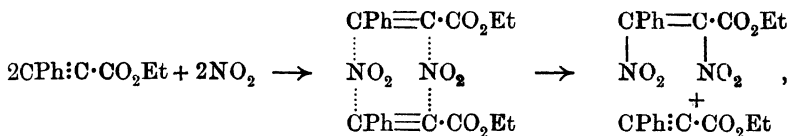
although it must be observed that no evidence is supplied as to the molecular weight of the intermediate compound.

It has also been found necessary to apply ideas of the kind referred to above to certain reactions of benzoxazole.[7] The ordinary formula (I) for this compound represents it as an imino-ether, which on hydrolysis would be expected to give an o-acylhydroxyaniline, whilst an o-acylaminophenol is actually obtained. It cannot be assumed that the compound (II) is first produced, since compounds of this type revert to oxazoles when heated:

(I.)   (II.)
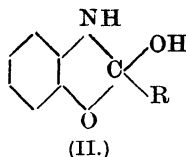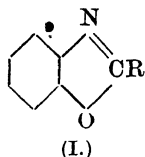
The change is therefore represented in the following manner:
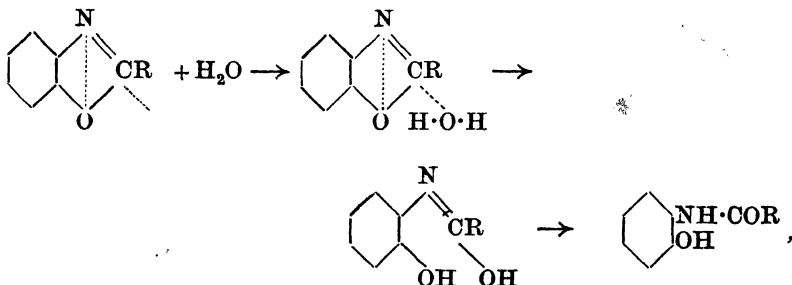
[6] H. Wieland, *Ber.*, 1920, **53**, [B], 1343; *A.*, i, 737.
[7] S. Skraup, *Annalen*, 1919, **419**, 1; *A.*, 1919, i, 598.

the decomposition of the intermediate product being attributed to the gradually increasing engagement of "valency lines" of the ring oxygen atom by one of the hydrogen atoms of the water molecule, and a consequent weakening of the cyclic structure. The velocity of hydrolysis is thus largely dependent on the rate of formation of the additive compound, which, in turn, varies with the amount of residual affinity available on the carbon atom after the requirements of the group R have been satisfied. The time required for 50 per cent. hydrolysis of various derivatives under standardised conditions is therefore considered to be some measure of the affinity of the group R. The following results were obtained:

R.	Time.	R.	Time.	R.	Time.
Benzyl.........	35 minutes	cycloHexyl...	5 hours	Phenyl	74 hours
Methyl.........	40 ,,	isoButyl......	5½ ,,	p-Tolyl......	more
n-Hexyl	3 hours	tert. ,, ...	7½ ,,	α-Naphthyl	than
				p-Anisyl ...	120 hours

It will be seen that the order of these measurements is in general agreement with those which may be deduced from observations of various other reactions.[8]

In yet another direction the results of a long series of investigations[9] are summed up as showing "how many factors influence ring-formation and rupture, and how little present-day formulæ suffice to explain the contradictory behaviour of apparently similarly constituted compounds." Thus, contrary to what might be expected, 1 : 1-dialkylcoumaranones, as well as the non-alkylated compounds, are apparently more stable than 1-alkyl derivatives, which frequently suffer rupture of the five-membered ring and give disemicarbazones instead of the monosemicarbazones obtained in other cases:
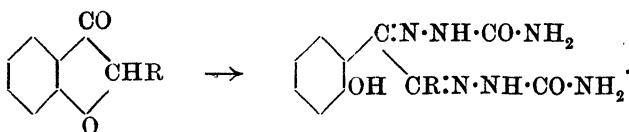
With p-nitrophenylhydrazine, however, coumaranones unsubstituted in the five-membered ring in general give osazones, this reac-

[8] Compare, for example, J. v. Braun, Ber., 1904, 37 , 2812, 2915; 1907, 40, 3914, 3933; 1909, 42, 2532; A., 1904, i, 731, 918; 1907, i, 899, 960; 1909, i, 604. H. Meerwein, Annalen, 1919, 419, 121; A., i, 2.

[9] K. von Auwers and others, ibid., 1908, 41, 4233; 1911, 44, 3692; 1914, 47, 2334, 2585, 3292; 1915, 48, 85; 1917, 50, 221, 1149; 1919, 52, [B], 77, 92; 1920, 53, [B], 428; Annalen, 1919, 418, 69; 1920, 421, 1; A., 1909, i, 45; 1912, i. 107; 1914, i, 1136; 1915, i, 154, 440, 442; 1917, i, 277; 1918, i, 27; 1919, i, 217; 1920, i, 866.

tion serving to distinguish them from chromanones, which give hydrazones :

$$\text{(CO, CH}_2\text{ benzofuranone)} \rightarrow \text{(C:N·NH·C}_6\text{H}_4\text{·NO}_2,\ \text{OH}\ \text{CH:N·NH·C}_6\text{H}_4\text{·NO}_2) ;$$

$$\text{(CO, CH}_2, \text{CH}_2, \text{O)} \qquad \text{(C·N·NH·C}_6\text{H}_4\text{·NO}_2,\ \text{CH}_2, \text{CH}_2, \text{O)}$$
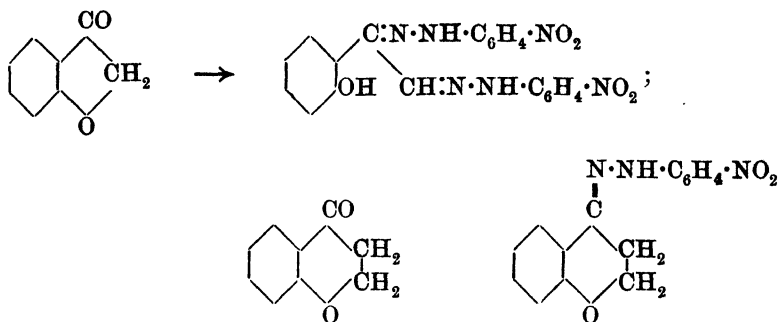
The only exception to this rule so far observed is 3 : 5-dimethyl-coumaranone, from which a hydrazone is obtained. The formation of 4-bromo-1 : 1 : 3 : 5-tetramethylcoumaranone as the sole product of the action of sodium hydroxide on α-bromo*iso*butyryl-4-bromo-*s*-xylenol is similarly in contrast with the production of 2 : 5-dimethyl-chromanone from α-bromo*iso*butyryl-*p*-cresol :

$$\text{Me, Br, CO·CBrMe}_2, \text{OH} \rightarrow \text{Me, Br, CO, CMe}_2, \text{O}$$

$$\text{Me, CO·CBrMe}_2, \text{OH} \rightarrow \text{Me, CO, CMe, OH, CH}_2 \rightarrow \text{Me, CO, CHMe, CH}_2, \text{O}$$
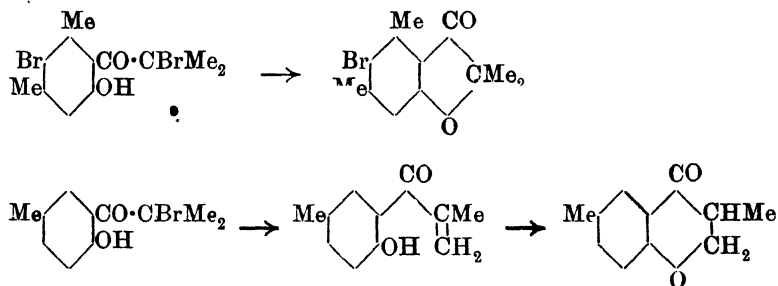
Whilst this exceptional behaviour on the part of *s*-xylenol derivatives recalls that observed in experiments on coupling [10] and in Friedel-Crafts syntheses,[11] and may be due to differences in the distribution of affinity, the experimental material at present available is insufficient to warrant the final adoption of this view.

Unsaturated compounds of the type indicated as an intermediate stage in the last of the above reactions form chromanones under the catalytic influence of alkali, as do their dibromides when alkali is employed to remove hydrogen bromide. On the other hand,

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[10] K. von Auwers and F. Michaelis, *Ber.*, 1914, **47**, 1275 ; K. von Auwers and E. Borsche, *Ber.*, 1915, **48**, 1716 ; *A.*, 1914, i, 744 ; 1916, i, 85.

[11] K. von Auwers and E. Borsche, *ibid.*, 1915, **48**, 1698 ; *A.*, 1916, i, 34.

coumarans are obtained from o-allylphenols and coumarones from the dibromides of their acetates by treatment with alkali [12]:
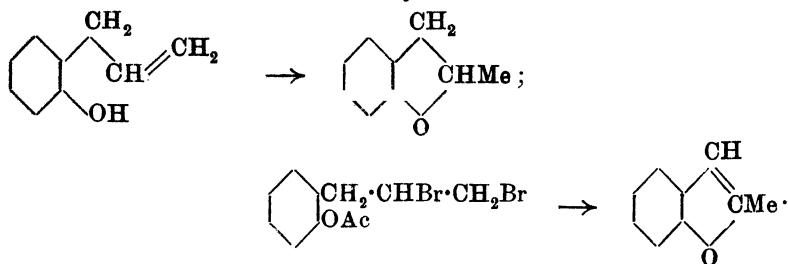
In explanation of this, it is suggested that the spatial configurations of the unsaturated side-chains in the two pairs of compounds differ, and are as represented in the formulæ.

Another notable reaction is that of 5-hydroxycoumarone-4-aldehyde, which is prepared from 5-hydroxy-2-methylcoumarone by the action of hydrocyanic acid in the presence of hydrogen chloride.[13] This compound, by condensation with acetic anhydride and sodium acetate, gives the corresponding acrylic acid.
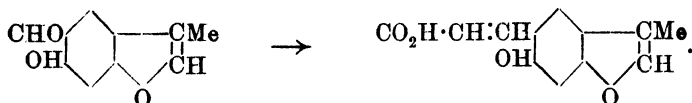
and all attempts to produce a coumarin from it by internal condensation failed. The result is attributed to steric hindrance, but supporters of the Kekulé formula for benzene will probably prefer to look upon it as evidence, confirming that of Marckwald adduced many years ago, of a difference in the mode of linking of the pairs of carbon atoms in the benzene nucleus.

The Stability and Formation of Cyclic Compounds.

The relative stability of various saturated cyclic structures, containing a tertiary nitrogen atom, towards cyanogen bromide and of their quaternary methylammonium hydroxides (Hofmann's degradation) has been carefully studied in recent years.[14] As a result it was found that the series tetrahydroisoquinoline, 1-methylmorpholine, dihydroisoindole, pyrrolidine, piperidine, and tetra-

[12] L. Claisen, Annalen, 1919, 418, 84; Ber., 1920, 53,, [B], 322; A., 1919, i, 266; 1920, i, 325; compare R. Adams and R. E. Rindfusz, J. Amer. Chem. Soc., 1919, 41, 648; A., 1919, i, 340.

[13] P. Karrer, A. Glattfelder, and F. Widmer, Helv. Chim. Acta, 1920, 3, 541; A., i, 627.

[14] J. von Braun, Ber., 1909, 42, 2035, 2532; 1911, 44, 1252; 1916, 49, 2629; 1918, 51, 96, 255; A., 1909, i, 604; 1911, i, 563; 1917, i, 168, 169; 1918, i, 185, 268.

hydroquinoline represented a gradual increase in stability for each reaction. Dihydroindole, however, one of the most reactive compounds towards cyanogen bromide, was the most resistent to the Hofmann reaction. The striking observation has now been made [15] that the nitrogen ring of the morphine molecule, which also contains the grouping ·C·C·N· attached by the first carbon atom to an aromatic nucleus, exhibits a similar divergence, but in the opposite direction. It is more stable in the first, and less stable in the second, reaction than any of the foregoing systems. Similar variations in the relative stabilities of a series of compounds towards different reagents have, of course, been observed in other directions. In considering them, it is perhaps well to remember that, in terms of the addition theory, the stabilities actually compared are rather those of the intermediate complexes, which are not necessarily in the order of those of the original compounds, and that differences may therefore well occur between the results obtained with different reagents. Furthermore, whilst the conclusions in respect of cyanogen bromide were obtained by comparative experiments on the separate compounds, a different method was followed in the case of the Hofmann reaction. For example, 1-o-vinylbenzylpiperidine was obtained by the distillation of " piperidyltetrahydroisoquinolinium hydroxide ":
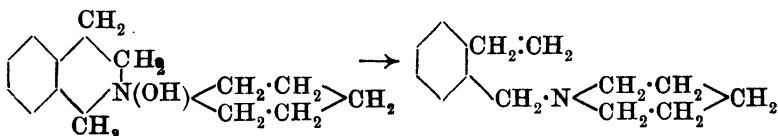
In this case, therefore, the piperidine is more stable than the tetrahydroisoquinoline ring, but a consideration of the results of the action of sodium amalgam on similar compounds [16] suggests doubts as to whether it is legitimate to extend this conclusion to pairs of compounds, one containing the piperidine ring, and the other the tetrahydroisoquinoline ring, and therefore as to whether a given ring structure in the various compounds containing it preserves precisely the same properties. Thus, from kairoline methochloride, kairoline (40 per cent.) and γ-phenylpropyldimethylamine (60 per cent.) are obtained:

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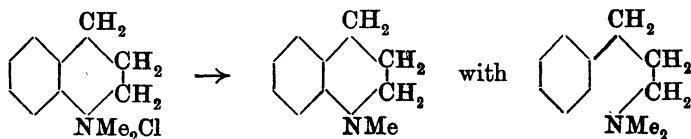
[15] *Idem, Ber.*, 1919, **52**, [B], 1999 ; *A.*, i, 79.

[16] J. v. Braun and others, *ibid.*, 1916, **49**, 501, 1283, 2613; 1917, **50**, 50 *A.*, 1916, i, 421, 742 ; 1917, i, 167, 282.

whilst N-methyldihydroindole (75 per cent.), β-phenylethyldimethyl-amine (8 per cent.), and o-ethyldimethylaniline (17 per cent.) are obtained from the methochloride of N-methyldihydroindole:

$$\begin{array}{c} CH_2 \\ | \\ CH_2 \\ | \\ NMe_2Cl \end{array} \longrightarrow \begin{array}{c} CH_2 \\ | \\ CH_2 \\ | \\ NMe \end{array} \text{ with }$$

$$\begin{array}{c} CH_2 \\ | \\ CH_2 \\ | \\ NMe \end{array} \text{ and } \begin{array}{c} CH_2 \\ | \\ CH_3 \\ | \\ NMe_2 \end{array}.$$
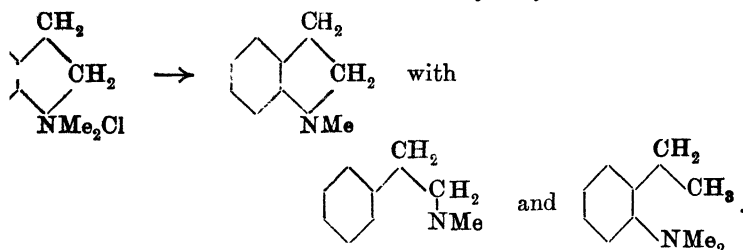
Yet lilolidine, prepared by boiling dihydroindole with 1-chloro-3-bromopropane, but not, be it noted, from tetrahydroquinoline and ethylene dibromide,[17] is not broken down by reduction of its methochloride. From 2-methyl-lilolidine the original base is recovered with a 10 per cent. yield of 1:2-dimethyl-7-n-propyldi-hydroindole [18]:

$$\begin{array}{c} CH_2 \cdot CHMe \\ | \\ NMeCl \\ CH_2 \\ CH_2 \\ CH_2 \end{array} \longrightarrow \begin{array}{c} CH_2 \cdot CHMe \\ | \\ N \\ CH_2 \\ CH_2 \\ CH_2 \end{array} \text{ with } \begin{array}{c} CH_2 \cdot CHMe \\ | \\ NMe \\ CH_3 \\ CH_2 \\ CH_2 \end{array}.$$
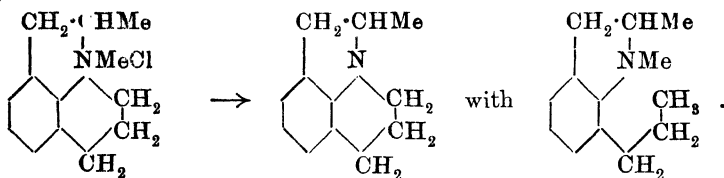
Cyclic Structures of New Types.

Results interesting in another respect have been obtained by the reduction of julolidine methochloride, from which the original base (63 per cent.) and the compound (I) (37 per cent.) are obtained [19]:

$$\begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \\ | \\ NMeCl \\ CH_2 \quad CH_2 \\ CH_2 \end{array} \longrightarrow \begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \\ | \\ N \\ CH \quad CH_2 \\ CH_2 \end{array} \text{ with }$$

$$\begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \\ | \\ NMe \\ CH_2 \quad CH_2 \\ CH_2 \end{array} \longrightarrow \begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2 \\ \\ CH_2 \cdot CH_2 \cdot CH_2 \cdot OH \end{array}$$

(I.) (II.)
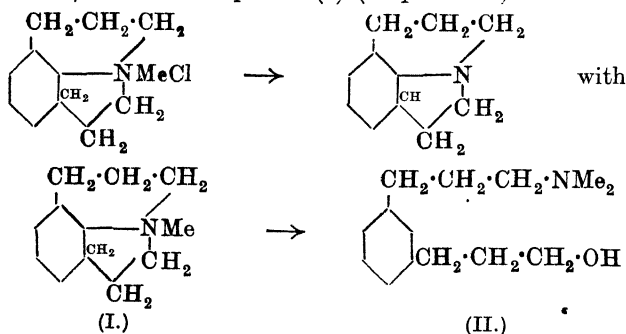
[17] E. Bamberger and H. Sternitzki, *Ber.*, 1893, **26**, 1291; *A.*, 1893, i, 520.

[18] J. v. Braun, K. Heider, and W. Wyczatkowska, *ibid.*, 1918, **51**, 1215; *A.*, 1919, i. 40.

[19] J. v. Braun and L. Neumann, *ibid.*, 1919, **52**, [B], 2015; *A.*, i, 87.

The constitution of the new base follows from its oxidation to *iso*-phthalic acid, and its degradation by the Hofmann reaction to a non-aromatic tertiary base (II), containing a non-phenolic hydroxyl group. Although the compound is unique in containing a ring structure attached to the benzene nucleus in the meta-position, very similar ten-membered rings attached in the ortho-position to benzene nuclei are contained in the products of the Hofmann reaction from tetrahydroberberine alkyl hydroxides,[20] and in crypto-pine and certain of its derivatives (compare p. 123).[21] It seems worthy of comment that all the products of this type hitherto obtained in the laboratory are produced, not synthetically, but by the breaking down of two simpler adjoining structures, and the easy conversion of the ten-membered ring of cryptopine into the two six-membered rings of *iso*cryptopine chloride suggests that in such ten-membered rings the carbon chain may preserve the con-figuration of the two rings from which it is derived. In spite, therefore, of the existence of the compounds in question, there is still room for doubt as to whether their synthesis, properly speaking, is possible.

A four-membered heterocyclic system of a new type appears to be present in the product of the action of nitrous acid on camphor-oxalic acid.[22] A transient blue colour suggests that the normal nitroso-compound (I) is first produced, but it gives place to a mono-basic acid, apparently according to the equation

$$\bullet C_{12}H_{15}O_5N + H_2O = C_{11}H_{17}O_4N + CO_2.$$
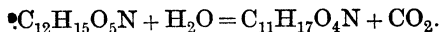
This acid gives a red coloration with ferric chloride, and hence contains an enolic grouping which, further, undergoes methylation before the carboxyl group. Although the acid is merely converted into what is probably a stereoisomeride by boiling concentrated potassium hydroxide solution, its dimethyl derivative is easily decomposed into ammonia and α-ketohomocamphoric acid (II). Further, the acid contains the complex $>N \cdot O \cdot$ as part of a ring, since it is easily reduced by ferrous hydroxide to camphidone-carboxylic acid (III). Although the nature of the changes

$$C_8H_{14}\left\langle \begin{array}{l} C(NO)\cdot CO\cdot CO_2H \\ CO \end{array} \right. \qquad C_8H_{14}\left\langle \begin{array}{l} CO\cdot CO_2H \\ CO_2H \end{array} \right.$$

(I.)   (II.)

$$C_8H_{14}\left\langle \begin{array}{l} CH(CO_2H) \\ \underline{\quad} CO \underline{\quad} \end{array} \right\rangle NH$$

(III.)
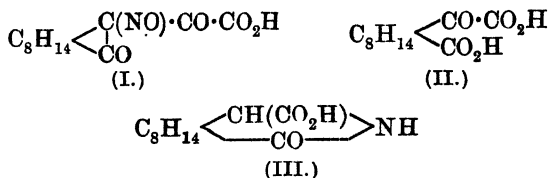
[20] F. L. Pyman, *T.*, 1913, **103**, 817.
[21] W. H. Perkin, *ibid.*, 1916, **109**, 815; 1919, **115**, 713.
[22] P. Chorley and A. Lapworth, *ibid.*, 1920, **117**, 728.

involved remains obscure, it is concluded that the original product contains the skeleton (IV), and of the alternatives which meet this condition, preference is given to that represented by (V).

$$C_8H_{14} \diagdown \overset{C \diagdown \underset{N}{C} \diagup O}{\underset{CO_2H}{}}$$ $$C_8H_{14} \diagdown \overset{C \diagdown \underset{-NH-}{C(OH)} \diagup O}{\underset{CO_2H}{}}$$

(IV.) (V.)
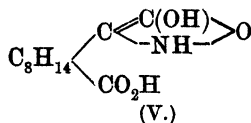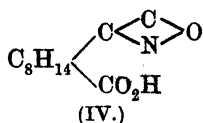
A Radicle containing Quadrivalent Nitrogen.

Dimethyl- and diethyl-tetrahydropyridyls[23] give yellowish-brown solutions in alcohol, which, especially in the presence of a little water or on warming, gradually become blue. In this condition they immediately absorb oxygen, with the formation of N-alkyl-pyridinium hydroxides, and give N-alkylpyridinium iodides with iodine.[24] The coloured solutions further resemble those of tri-phenylmethyl in their diminished colour intensity at lower temperatures. Although no molecular weight determinations are quoted, it is concluded that dissociation occurs, and that the coloured solute is a radicle containing quadrivalent nitrogen rather than tervalent carbon:
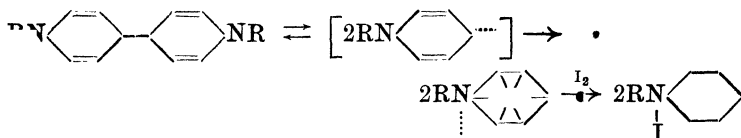
The latter may possibly be present in the yellow, ethereal solution or the pale green chloroform solution, since these give a yellow, amorphous product with iodine.

The dissociation is ascribed to the weakening effect of the various double bonds on the valencies of the γ-carbon atoms, but there is no discussion of the meaning, or the nature, of the change from tervalent carbon to quadrivalent nitrogen.

Stereoisomerism of Tervalent Nitrogen Compounds.

Well-defined stereoisomerism of tervalent nitrogen compounds has hitherto been observed only in the case of compounds, such as oximes, in which, according to the usual formulæ, the directions of two valencies are fixed by a double bond, and reference will be

[23] A. W. Hofmann, *Ber.*, 1881, **14**, 1503; *A.*, 1881, 921; compare B. Emmert, *Ber.*, 1909, **42**, 1997; 1917, **50**, 31; 1919, **52**, [B], 1351; *A.*, 1909, i, 602; 1917, i, 221; 1919, i, 455.

[24] B. Emmert, *ibid.*, 1920, **53**, [B], 370; *A.*, i, 331.

made later to the first case of such isomerism observed among the hydrazones. A number of cases have, however, now been observed in which the directions of the two valencies are defined by participation of the nitrogen atom in a cyclic structure.

A closer examination of the isomerism of methyl*iso*pelletierine (I) and *dl*-methylconhydrinone (II), referred to in last year's Report, has confirmed it, and led to the discovery of further examples.[25] *iso*Pelletierine (III), which occurs naturally, and can also be obtained by the demethylation of methyl*iso*pelletierine, on re-methylation gives methyl*iso*pelletierine alone, thus differing from *dl*-conhydrinone (IV), which gives both this compound and *dl*-methylconhydrinone. Further, whilst *iso*pelletierine is recovered from its carboxylic ester (V) on alkaline hydrolysis, the corresponding derivative of *dl*-conhydrinone (VI) undergoes a remarkable reaction, which may have a significance in connexion with the processes of plant life, α-2-pyrrolidylbutan-β-one (VII) being produced in excellent yield. It is seen that these results are

explicable on the basis of the configurations indicated, and originally assigned to the first pair of isomerides, on the ground of the failure through steric hindrance of *dl*-methylconhydrinone to react with semicarbazide, and its slower reaction with hydroxylamine and hydrazine. The isomerism in question is preserved when methyl *iso*pelletierine and *dl*-methylconhydrinone are reduced to the corresponding amino-alcohols, a distinct pair of products being obtained from each. The ketonic group is there-

[25] K. Hess, *Ber.*, 1919, **52**, [B], 1622; 1920, **53**, [B], 129; *A.*, i, 86, 329.

forms not essential to the isomerism, but the formation of the same *dl*-methylconiine from both series suggests that the oxygen atom may be in the present instance. This, however, is apparently not always so, because the isomeric forms of 1-methyl-2-propyl(or *iso*-butyl or benzyl)-tetrahydroquinoline [26] resemble the above compounds in giving different quaternary ammonium salts, and are probably examples of the same type of isomerism.

The considerable difference in properties exhibited by the various pairs of isomerides is in marked contrast to the close agreement between coniine and *iso*coniine. This, in conjunction with the production of the same methylconiine from the above isomerides, suggests doubts as to the reality of their isomerism, and a careful investigation [27] has now shown that *iso*coniine is merely a slightly impure form of coniine

A whole series of stereoisomerides has been discovered among the 2-acidyl derivatives of indazole.[28] Stable compounds are obtained by the action of acetic, propionic, or benzoic anhydrides on indazole, or its derivatives containing substituents in the benzene nucleus. From acid chlorides, however, and either the parent substances in presence of pyridine or their silver salts alone, labile isomerides are produced which more or less readily pass over into the stable forms. The inherent improbability of such a formula as (I) excludes an explanation based on structural isomerism, whilst the recovery of each from its double compounds

(I.)   (II.)   (III.)

(IV.)   (V.)
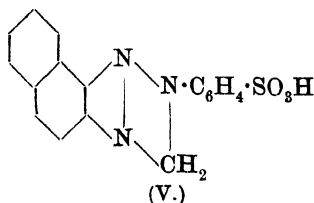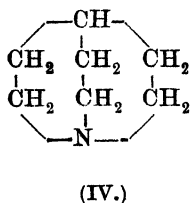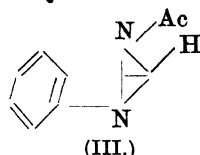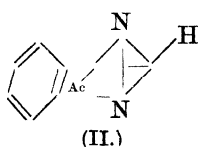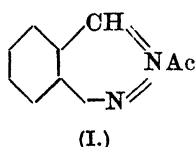
with, for example, mercuric chloride shows that these are not cases of physical isomerism. It is therefore suggested that the relationship between them is represented by the formulæ (II) and

[26] M. Freund and E. Kessler, *J. pr. Chem.*, 1918, [ii], **98**, 233; *A.*, 1919, i, 283.

[27] K. Hess and W. Weltzien, *Ber.*, 1920, **53**, [B], 139; *A.*, i, 330.

[28] K. von Auwers and M. Düesberg, *ibid.*, 1179; *A.*, i, 638.

(III). The analogy to the oximes suggested by these formulæ is strengthened by the fact that, as with acetophenoneoxime, so in the case of 2-acidyl derivatives of 3-methylindazole, only one form has been isolated. Pursuing this, the labile acidyl-indazoles are regarded as *syn-* (III) and the stable forms as *anti*-compounds (II).

In quinuclidine (IV), the three valencies of the nitrogen atom are fixed and directed towards the corners of a tetrahedron. The prediction is therefore made that it should be possible to obtain suitably chosen substitution derivatives in enantiomorphous forms, but experimental work in this direction has not got beyond the initial stages.[29] Its development will be awaited with interest, because the same conditions are present in 2-*p*-sulphophenyl-2:3-dihydro-1:2:4-naphtha*iso*triazine (V), the apparent resolution of which was reported some years ago.[30]

The optical activity of pelletierine and methyl*iso*pelletierine has been reaffirmed.[31]

Symmetric and Asymmetric Synthesis.

Consequent upon the elucidation of the structure of scopoline (p. 127), an interesting discussion[32] has developed as to the processes by which in plant life racemic mixtures, such as coniine, methylconiine, pelletierine, *iso*pelletierine, methyl*iso*pelletierine, atropine, laudanine, scopoline, paricine, cryptopine, arabine, cevadine, delphinine, and delphinidine, are sometimes produced. In the majority of these cases it is not unreasonable to assume that at some stage in their synthesis a process occurs independently of the plant organism, which is a symmetrical one. Thus *dl*-coniine (II) may possibly be produced by such a process from optically active conhydrin (I):

$$
\begin{array}{ccc}
\mathrm{CH_2} & \mathrm{CH_2} & \mathrm{CH_2} \\
\mathrm{CH_2\ CH_2} & \mathrm{CH_2\ CH_2} & \mathrm{CH_2\ CH_2} \\
\mathrm{CH_2\ CH\cdot CHEt\cdot OH} & \mathrm{CH_2\ C{:}CHEt} & \mathrm{CH_2\ CH\cdot CH_2Et} \\
\mathrm{NH} & \mathrm{NH} & \mathrm{NH} \\
\textbf{(I.)} & & \textbf{(II.)}
\end{array}
$$
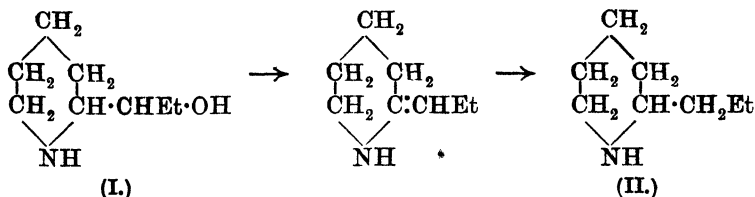
It seems, however, improbable that such a hypothesis can apply to the case of scopoline, because four asymmetric carbon atoms are

[29] J. Meisenheimer, *Annalen*, 1920, **420**, 190; *A.*, i, 761.
[30] T. S. Moore, *P.*, 1914, **30**, 182.
[31] G. Tanret, *Compt. rend.*, 1920, **170**, 1118; *A.*, i, 499.
[32] K. Hess and W. Weltzien, *Ber.*, 1920, **53**, [B], 119; H. Pringsheim, *ibid.*, 1375; K. Hess, *ibid.*, 1375; *A.*, i, 328, 774.

involved, and it would become necessary to assume that the majority of the stages of its formation are spontaneous processes. The conclusion therefore seems inevitable that the plant organism is capable of symmetric synthesis. Although cases of this kind are not entirely unknown in animal life, for example, the presence of *dl*-arabinose in urine as a result of certain disorders,[33] they are very exceptional. It appears, therefore, that the specific action of enzymes is considerably more pronounced in animal than in plant life.

Catechin.

The constitution of catechin has now been practically determined as a result of the study[34] of the methylated product of reduction of catechin tetramethyl ether,[35] which, on oxidation with alkaline permanganate, furnishes an acid, the molecule of which contains one atom of carbon less. Since this degradation is found to be common to compounds containing the ethyl group:

$$R \cdot CH_2 \cdot CH_3 \longrightarrow R \cdot CO_2H,$$
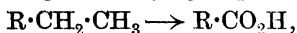
it would appear that the reduction product is $3:4:2':4':6'$-pentamethoxy-$\alpha\alpha$-diphenylpropane (A), which on oxidation would give $3:4:2':4':6'$-diphenylacetic acid (B), and these conclusions have been verified by synthesis. The acid was obtained from

(I.)   (A.)   (B.)
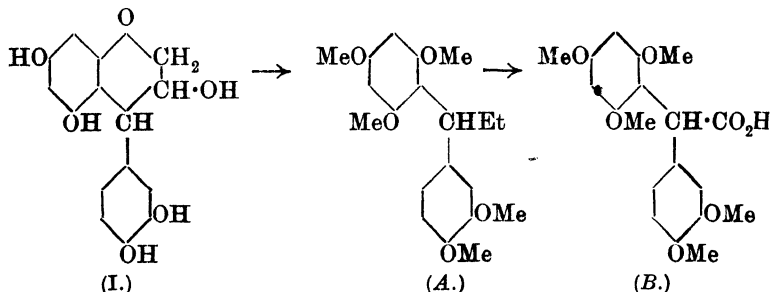
$3:4:2':4':6'$-pentamethoxydiphenylcarbinol through the corresponding chloride by means of the Grignard reaction. From its chloride and diazomethane, $3:4:2':4':6'$-pentamethoxydiphenylmethyl chloromethyl ketone is obtained, which by reduction is converted into the required propane derivative:

$$C_6H_2(OMe)_3 \cdot CH(OH) \cdot C_6H_3(OMe)_2 \longrightarrow$$
$$C_6H_2(OMe)_3 \cdot CH(CO_2H) \cdot C_6H_3(OMe)_2 \longrightarrow$$
$$C_6H_2(OMe)_3 \cdot CH(CO \cdot CH_2Cl) \cdot C_6H_3(OMe)_2 \longrightarrow$$
$$C_6H_2(OMe)_3 \cdot CHEt \cdot C_6H_3(OMe)_2.$$
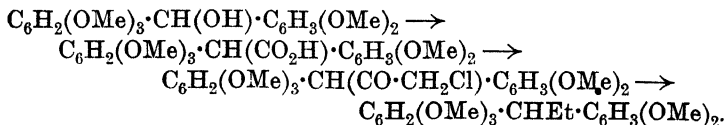
[33] Compare C. Neuberg, *Ber.*, 1900, **33**, 2243; 1902, **35**, 1468; *A.*, 1900, i, 539; 1902, ii, 417.   [34] M. Nierenstein, *T.*, 1920, **117**, 971, 1151.
[35] S. von Kostanecki and V. Lampe, *Ber.*, 1907, **40**, 720; *A.*, 1907, i, 334.

The properties of each of these compounds are in accordance with anticipation, and the formula (I) is proposed for catechin, in place of the older formulæ (II) [36] and (III),[37] according to which the product referred to above would be either 2:4:6:3′:4′-pentameth-oxy-3-ethyldiphenylmethane (IV) or 3:4:2′:4′:6′-pentamethoxy-αγ-diphenylpropane (V). Each of these compounds has been syn-thesised by the reduction of 2:4:6:3′:4′-pentamethoxy-3-ethyl-benzophenone and 2:4:6-trimethoxyphenyl 3:4-dimethoxystyryl ketone respectively, and found to differ from the compound in

(II.) → (IV.)

(III.) → (V.)
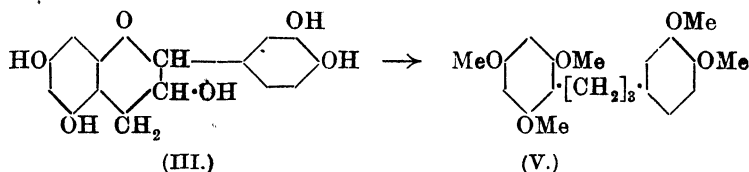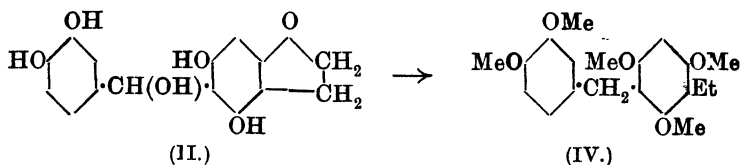
question. Finally, in confirmation of the new formula, reduction of 3-phenylchroman (VI) results in the formation of 2-hydroxy-αα-diphenylpropane (VII), from which 2-hydroxydiphenylacetic acid (VIII) is obtained on oxidation with potassium permanganate.

(VI.) → (VII.) → (VIII.)

(IX.) → (X.)
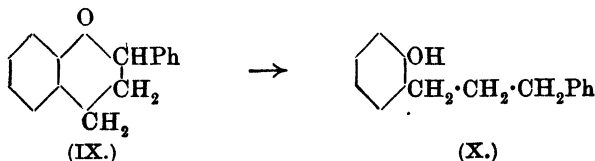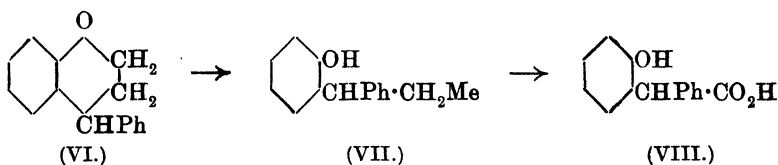
From 1-phenylchroman (IX), 2-hydroxy-αγ-diphenylpropane (X) is obtained, and found to be stable towards permanganate.[38]

[36] S. von Kostanecki and V. Lampe, *Ber.*, 1907, **40**, 720; *A.*, 1907, i, 334.

[37] A. G. Perkin and E. Yoshitake, *T.*, 1902, **81**, 1172; compare H. Ryan and M. J. Walsh, *Sci. Proc. Roy. Dub. Soc.*, 1916, **15**, 113; *A.*, 1916, i, 722.

[38] (Miss) A. Greenwood and M. Nierenstein, *T.*, 1920, **117**, 1594.

The evidence is therefore so complete that it suffices merely to refer to another investigation,[38a] in which the identity is affirmed of the methylated reduction product with pentamethoxy-αγ-diphenyl-propane, although, remarkably enough, in other respects substantially the same account is given of the preparation and properties of this compound. In the circumstances, also, less interest attaches to experiments on the synthesis of compounds,[39] the structure of which is in close agreement with the formula (II). Thus, by the respective condensations of 5-hydroxy-2-methylcoumarone and 5-hydroxy-2-methylcoumaran with benzonitrile in the presence of hydrogen chloride, 5-hydroxy-2-methyldepsenone (I) and 5-hydroxy-2-methyldepsanone (II) are obtained, and from these by reduction the corresponding secondary alcohols:

(I.)

(II.)
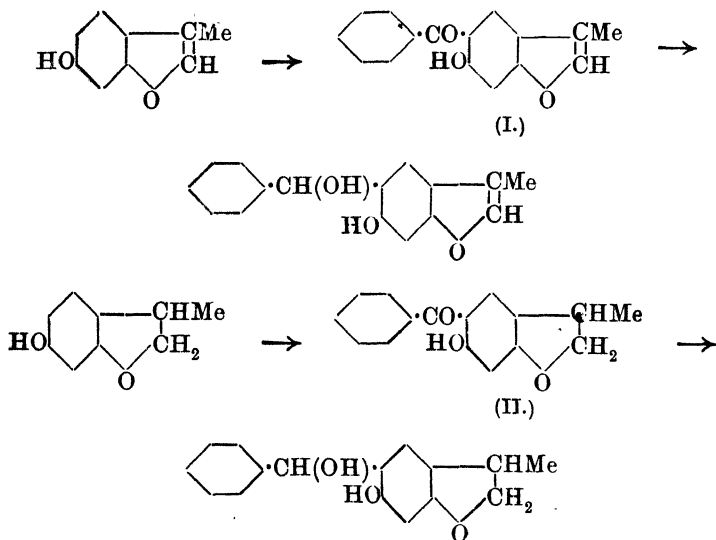
The Anthocyanins.

The evidence for the constitution of the anthocyanins, recorded some years ago,[40] was rounded off by a synthesis of pelargonidine described in a paper,[41] which, however, has only recently become available in this country. By condensation of 2 : 4 : 6-trihydroxy-

[38a] K. Freudenberg, *Ber.*, 1920, **53**, [B], 1416; *A.*, i, 752.

[39] P. Karrer and F. Widmer, *Helv. Chim. Acta*, 1919, **2**, 454; *A.*, 1919, i, 595.

[40] Compare *Ann. Reports*, 1914, **11**, 138; 1915, **12**, 156.

[41] R. Willstätter and L. Zechmeister, *Sitzungsber.' Preuss. Akad. Wiss. Berlin*, 1914, **34**, 886; *A.*, i, 561.

benzaldehyde with sodium methoxyacetate and the corresponding anhydride, 5:7-dimethoxyacetoxy-3-methoxycoumarin (I) is obtained. This compound, by successive treatment with sodium hydroxide and diazomethane, gives 3:5:7-trimethoxycoumarin (II), which reacts with magnesium p-anisyl bromide to form 3:5:7-trimethoxy-2-p-anisylpyrylium chloride (III), from which the methyl groups are removed by means of hydriodic acid. From the iodide thus produced a chloride (IV) is obtained, which is identical in every respect with that of natural pelargonidine [42]:

(I.) (II.)

(III.) (IV.)
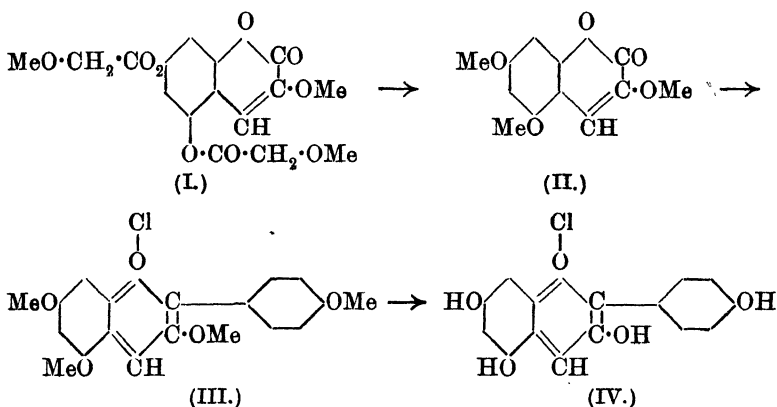
Some other Plant Products.

Anemonin (I), which is obtained with anemonic acid and protoanemonin by the steam distillation of certain varieties of *Anemone* and *Ranunculus* [43] has now been shown to be an unsaturated lactone. It is a doubly unsaturated compound of the formula $C_{10}H_8O_4$, which exhibits the reactions of the carbonyl group,[44] yields oxalic and succinic acids on oxidation, and by acid or alkaline hydrolysis is converted into anemoninic acid (II). The last is an unsaturated compound, with reducing properties and existing in stereoisomeric forms, which gives γ-ketopimelic acid on oxidation. By catalytic reduction of anemonin,[45] a tetrahydro-derivative (III) and, finally, sebacic acid are produced, whilst a dihydro-derivative (IV) is produced in the presence of sodium amalgam, and this is converted by hydrolysis into anemonolic acid, which is found to be identical with diæevulic acid (V), and is obtained directly from anemonin by the

[42] R. Willstätter and E. K. Bolton, *Annalen*, 1915, **408**, 42; *A.*, 1915, i, 283.
[43] H. Beckurts, *Chem. Zentr.*, 1885, 776; *A.*, 1886, 365.
[44] *Ibid.*, *Arch. Pharm.*, 1892, **230**, 182; *A.*, 1892, 1241.
[45] Y. Asahina and A. Fujita, *J. Pharm. Soc. Japan*, 1919, 471; 1920, 1; 1920, No. 461; *A.*, i, 70, 493, 678.

action of cold hydriodic acid. The changes are represented by the following scheme:

$$
\underset{(\text{I.})}{\begin{array}{c} CH_2 \cdot C \!\!<\!\! \begin{array}{c} CH\!:\!CH \\ O\!-\!CO \end{array} \\ | \\ CH_2 \cdot C \!\!<\!\! \begin{array}{c} CH\!:\!CH \\ O\!-\!CO \end{array} \end{array}}
\rightarrow
\underset{(\text{IV.})}{\begin{array}{c} CH_2 \cdot C \!\!<\!\! \begin{array}{c} CH \cdot CH_2 \\ O\!-\!CO \end{array} \\ | \\ CH_2 \cdot C \!\!<\!\! \begin{array}{c} CH \cdot CH_2 \\ O\!-\!CO \end{array} \end{array}}
\rightarrow
\underset{(\text{III.})}{\begin{array}{c} CH_2 \cdot C \!\!<\!\! \begin{array}{c} CH_2 \cdot CH_2 \\ O\!-\!CO \end{array} \\ | \\ CH_2 \cdot C \!\!<\!\! \begin{array}{c} CH_2 \cdot CH_2 \\ O\!-\!CO \end{array} \end{array}}
$$

Sebacic acid

$$
\underset{(\text{II.})}{\begin{array}{c} CH_2 \cdot CO \cdot CH\!:\!CH \cdot CO_2H \\ CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H \end{array}}
\qquad
\underset{(\text{V.})}{\begin{array}{c} CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H \\ CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H \end{array}}
$$
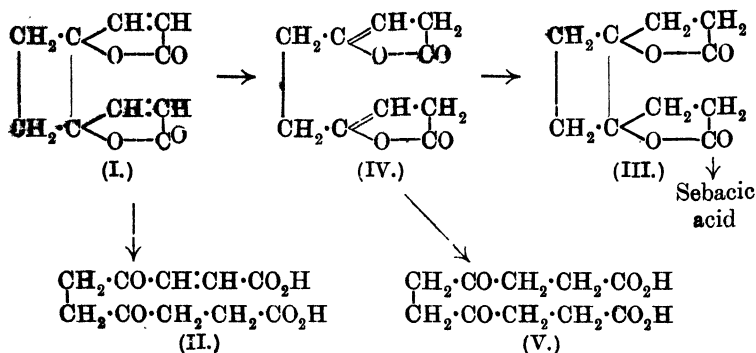
This interpretation is supported by the synthesis of protoanemonin (VI), a vesicant substance from which anemonin is derived by spontaneous polymerisation. Acetylation of β-bromolævulic acid results in the formation of a lactone (VII), from which the elements of hydrogen bromide are removed by means of sodium acetate. The product, doubtless acetylacetoacrylic acid, on distillation furnishes protoanemonin:

$$
CH_3 \cdot CO \cdot CHBr \cdot CH_2 \cdot CO_2H
\rightarrow
\underset{(\text{VII.})}{\begin{array}{c} CH_3 \\ AcO \end{array}\!\!>\!\!C\!\!<\!\! \begin{array}{c} CHBr \cdot CH_2 \\ O\!-\!CO \end{array}}
\rightarrow
$$

$$
\left[\begin{array}{c} CH_3 \\ AcO \end{array}\!\!>\!\!C\!\!<\!\! \begin{array}{c} CH\!:\!CH \\ O\!-\!CO \end{array} \right]
\rightarrow
\underset{(\text{VI.})}{\begin{array}{c} CH_2\!:\!C\!\!<\!\! \begin{array}{c} CH\!:\!CH \\ O\!-\!CO \end{array} \end{array}}
$$
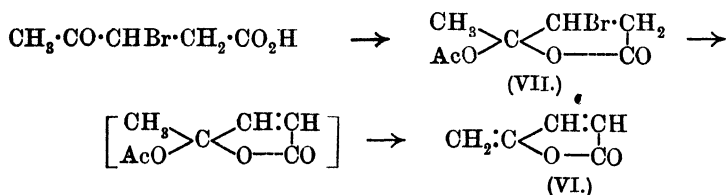
Anemonin has been similarly synthesised from dibromoangelica-lactone.

Hyptolide, another plant product, is also considered to be an unsaturated lactone, and is formulated as a derivative of dihydropyrone [46]:

$$
\begin{array}{c} CH \cdot CMe_2 \\ CH \cdot CO \cdot O \end{array}\!\!>\!\!CMe \cdot [CH \cdot OAc]_3 \cdot CH_3.
$$
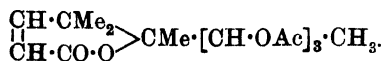
Elsholtzione, a ketone, $C_{10}H_{14}O_2$, obtained by steam distillation of *Elsholtzia cristata*,[47] yields *iso*valeric acid on oxidation, and by treatment with amyl nitrite and sodium ethoxide is degraded to 3-methylfuran-2-carboxylic acid (homopyromucic acid), a behaviour which is reproduced by the synthetic ketones obtained

[46] K. Gorter, *Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 327; *A.*, i, 494.
[47] Y. Asahina and Y. Murayama, *Arch. Pharm.*, 1914, **252**, 435; *A.*, 1915, i, 429.

by the action of magnesium alkyl haloids on pyromuconitrile. These reactions and the reduction of its hydrazone to 3-methyl-2-*iso*amylfuran (II) all point to the composition of the compound as being represented by the formula (I).[48]

$$
\begin{array}{ccc}
\text{CH–CMe} & & \text{CH–CMe} \\
\text{CH} \quad \text{C·CO·CH}_2\text{·CHMe}_2 & \rightarrow & \text{CH} \quad \text{C·C(:N·NH}_2\text{)·CH}_2\text{·CHMe}_2 \rightarrow \\
\diagdown\diagup & & \diagdown\diagup \\
\text{O} & & \text{O}
\end{array}
$$

$$(\text{I.})$$

$$
\begin{array}{c}
\text{CH–CMe} \\
\text{CH} \quad \text{C·CH}_2\text{·CH}_2\text{·CHMe}_2 \\
\diagdown\diagup \\
\text{O}
\end{array}
$$

$$(\text{II.})$$
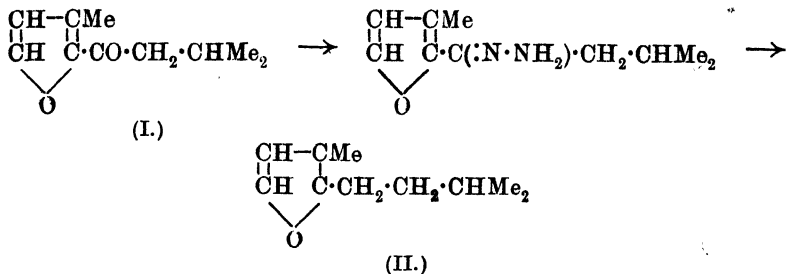
The Glyoxalines.

An investigation of· the orientation of substitution derivatives of glyoxaline has given interesting results. Direct nitration,[49] and probably also direct sulphonation,[50] takes place in the 4-position. On reduction by cold stannous chloride solution, the 4-nitro-derivatives of 5- and 2-methylglyoxalines, and of glyoxaline itself, respectively give, not the amino-compounds (a small proportion in the case of the 5-methyl derivative being excepted), but α-alanine, α-amino-α-iminoethane, and glycine. The course of the changes in the last two cases is represented as follows: [51]

$$
\begin{array}{lcl}
(a) & \underset{\text{NO}_2\text{·C}}{\overset{\text{CH·NH}}{\diagup}}\!\!\!\!\underset{\text{—N}}{\diagup}\!\!\!\!\diagdown\text{CMe} & \rightarrow \quad \left[\underset{\text{NH}_2\text{·C}}{\overset{\text{CH·NH}}{\diagup}}\!\!\!\!\underset{\text{—N}}{\diagup}\!\!\!\!\diagdown\text{CMe}\right] \rightarrow \\
\end{array}
$$

$$
\left[\underset{\text{CO}}{\overset{\text{CH}_2\text{·NH}}{\diagup}}\!\!\!\!\underset{\text{—N}}{}\!\!\diagdown\text{CMe}\right] \quad \rightarrow \quad \underset{\text{HN}}{\overset{\text{NH}_2}{\diagdown}}\!\!\diagdown\text{CMe}
$$

$$
\begin{array}{lcl}
(b) & \underset{\text{NO}_2\text{·C}}{\overset{\text{CH·NH}}{\diagup}}\!\!\!\!\underset{\text{—N}}{\diagup}\!\!\!\!\diagdown\text{CH} & \rightarrow \quad \left[\underset{\text{NH}_2\text{·C}}{\overset{\text{CH·NH}}{\diagup}}\!\!\!\!\underset{\text{—N}}{\diagup}\!\!\!\!\diagdown\text{CH}\right] \rightarrow \\
\end{array}
$$

$$
\left[\underset{\text{CO}}{\overset{\text{CH}_2\text{·NH}}{\diagup}}\!\!\!\!\underset{\text{—N}}{}\!\!\diagdown\text{CH}\right] \quad \rightarrow \quad \underset{\text{CO}_2\text{H}}{\overset{\text{CH}_2\text{·NH}_2}{}}.
$$
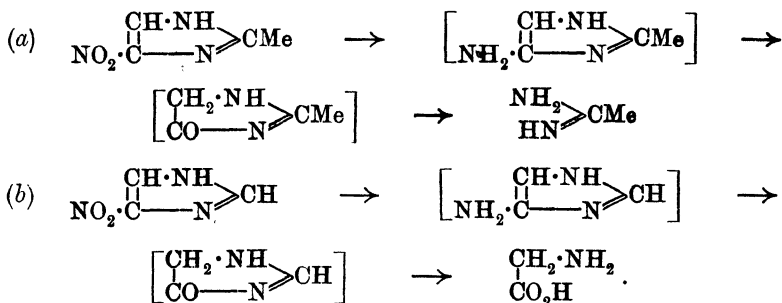
Although this is a plausible view of the reaction, it seems not very clear by what process the amino-compounds are converted into glyoxalones. The hypothesis, which may first suggest itself to the

[48] M. Asano, *J. Pharm. Soc. Japan*, 1919, 999 ; *A*., i, 495.

[49] R. G. Fargher and F. L. Pyman, *T*., 1919, **115**, 217.

[50] F. L. Pyman and L. A. Ravald, *ibid*., 1920, **117**, 1429.

[51] R. G. Fargher, *ibid*., 668.

reader and ascribe the change to a hydrolysis of the amino-deriv-ative reacting in the imino-form, would probably not be accept-able, because 4-amino-5-methylglyoxaline shows the reactions of a true amine, whilst 2-aminoglyoxaline is a monoacidic, non-diazotisable base, which does not give a benzylidene derivative. It is therefore regarded as an imino-compound, although in this case its stability towards acid may seem remarkable.

The Rhodanines.

The results of two investigations point to the existence of tautomerism in the rhodanine series. Thus, whilst rhodanine gives a colourless dibenzoyl derivative (I), a yellow monobenzoyl derivative (II) is obtained from benzylidenerhodanine.[52] Further,

$$S\!<\!\begin{array}{l} C(SBz)\!:\!N \\ CH\!=\!\!=\!\!C\cdot OBz \end{array}$$

(I.)

$$S\!<\!\begin{array}{l} C(SBz)\!=\!\!=\!N \\ C(:CHPh)\cdot CO \end{array}$$

(II.)
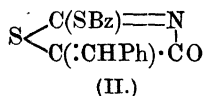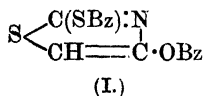
5-methyl-3-ethylrhodanine-5-acetic acid (III) is obtained in an optically active form by the condensation of sodium l-methyl-bromosuccinate with potassium ethyldithiocarbamate, but 3-phenyl-5-methylrhodanine (IV), prepared from phenylthiocarbamide and d-thiol-lactic acid, is inactive, owing to racemisation of the initial product through its enolic form.[53]

$$S\!<\!\begin{array}{l} CS\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!NEt \\ CMe(CH_2\cdot CO_2H)\cdot CO \end{array}$$

(III.)

$$S\!<\!\begin{array}{l} CS\!-\!\!-\!\!-\!NPh \\ CHMe\cdot CO \end{array}$$

(IV.)
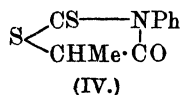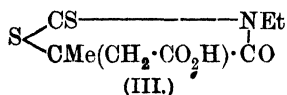
The Quinoline Group.

The well-known reactivity of 2- and 4-substituents in the pyridine nucleus is further exemplified by the preparation of α- and γ-quinolinesulphonic acids by boiling the corresponding chloro-compounds with a solution of sodium hydrogen sulphite.[54] Similarly, the acids, which may also be prepared from the thio-quinolines, on treatment with phosphorus pentachloride give, not the corresponding sulphonyl chlorides, but the chloroquinolines, and the α-sulphonic acid is converted into carbostyril by simply boiling it with water. The β-isomeride, which is obtained in an

[52] C. Gränacher, Helv. Chim. Acta, 1920, 3, 152; A., i, 252.
[53] S. Kallenberg, Ber., 1919, 52, [B], 2057; A., i, 90.
[54] E. Besthorn and B. Geisselbrecht, ibid., 1920, 53, [B], 1017; A., i, 563.

indirect manner, is a stable compound, from which a sulphonyl chloride can be prepared in the usual way.

The total synthesis of quinine and its derivatives is nearing completion, since methods are now available for dealing with particular cases of each stage of the problem. As these may well prove adequate for the purpose in view, it seems appropriate to indicate briefly the present position.

(a) The syntheses of quinic and cinchonic acids from quinoline and methoxyquinoline, respectively, have been referred to in previous Reports,[55] whilst the communication is promised of results obtained by the use of Knorr's quinoline synthesis.[56]

(b) For the preparation of appropriate derivatives of β-4-piperidylpropionic acid, hitherto certain less valuable alkaloids of the cinchonine group have been subjected to degradation. For example, cinchotine (dihydrocinchonine) (I) is converted into cinchoticine (cinchotoxine) (II). The dimethosulphate of N-benzoylcinchotoxine (III) is then converted by oxidation to

$$CHEt \cdot CH\!-\!CH_2$$
$$\mid \quad CH_2 \quad \mid$$
$$\mid \quad CH_2 \quad \mid$$
$$CH_2\!-\!N\!-\!\!-\!CH$$
$$CH \cdot OH$$

(I.)

$$CHEt \cdot CH\!-\!CH_2$$
$$\mid \quad CH_2 \quad \mid$$
$$\mid \quad CH_2 \quad \mid$$
$$CH_2\!-\!NH \quad CH_2$$
$$CO$$

(II.)

$$CHEt \cdot CH\!-\!CH_2$$
$$\mid \quad CH_2 \quad \mid$$
$$\mid \quad CH_2 \quad \mid$$
$$CH_2\!-\!\!-\!NBz \quad CH_2$$
$$CO$$

$$NMe_2SO_4$$

(III.)

$$CHEt \cdot CH\!-\!CH_2$$
$$\mid \quad CH_2 \quad \mid$$
$$\mid \quad CH_2 \quad CH_2$$
$$CH_2\!-\!NBz \quad CO_2H$$

(IV.)

$$+ \quad CO_2H$$
$$NMe \cdot CHO$$
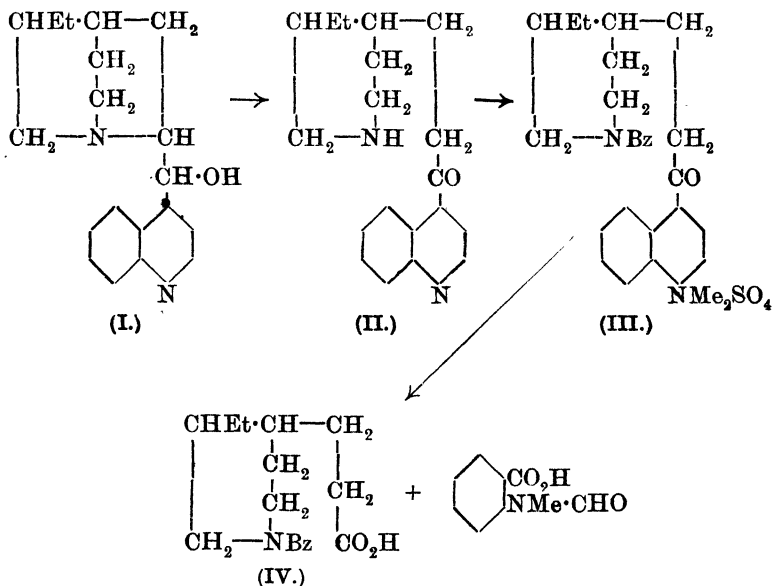
N-benzoylhomocincholoeupone (IV).[57] The synthesis proper of these acids is now foreshadowed by that of the parent β-4-piperidyl-

[55] *Ann. Reports*, 1918, **15**, 113; 1911, **8**, 142.

[56] P. Rabe and K. Kindler, *Ber.*, 1918, **51**, 1360; *A.*, 1919, i, 34.

[57] A. Kaufmann, E. Rothlin, and P. Brunnschweiler, *ibid.*, 1916, **49**, 2299; *A.*, 1917, i, 50; P. Rabe and K. Kindler, *loc. cit.*

propionic acid as the product of reduction of β-4-pyridylacrylic acid, which may be obtained from γ-picoline and chloral:

Me
$CH_2 \cdot CH(OH) \cdot CCl_3$
$CH:CH \cdot CO_2H$

$CH \cdot CH_2 \cdot CH_2 \cdot CO_2H$

$$H_2C \diagdown CH_2$$
$$H_3C \diagup CH_2$$
NH
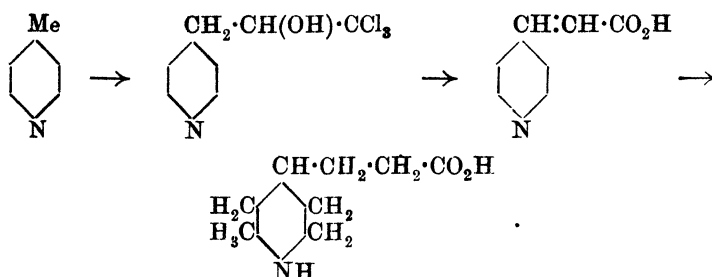
Since it has also been found possible to convert nicotinic acid into β-ethylpyridine,[58] there is a good prospect of preparing homo-cincholeupone from γ-picoline-β-carboxylic acid, which itself is accessible by synthesis. Owing, however, to the presence of two asymmetric carbon atoms in the formula, the synthetic product will consist of four isomerides, of which only one will serve for the synthesis of the natural alkaloids. Further, special precautions will, of course, be required in connexion with the unsaturated group when the attempt is made to synthesise homomeroquinenine, from which cinchonine and quinine themselves are derived.

(c) The condensation of ethyl cinchonate or ethyl quinate with ethyl N-benzoylhomocincholeupone by means of the Claisen reaction, and subsequent elimination of the benzoyl and carbethoxyl groups, has resulted in the respective syntheses of dihydro-cinchoticine [59] (I) and dihydroquinicine,[59a] which have been con-

$$C_9H_6N \cdot CO_2Et + CO_2Et \cdot CH_2 \cdot CH_2 \cdot CH \diagup CH_2 - CH_2 \diagdown NBz \longrightarrow$$
$$CHEt \cdot CH_2$$

$$C_9H_6N \cdot CO \cdot CH(CO_2Et) \cdot CH_2 \cdot CH \diagup CH_2 - CH_2 \diagdown NBz \longrightarrow$$
$$CHEt \cdot CH_2$$

$$C_9H_6N \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH \diagup CH_2 - CH_2 \diagdown NH$$
$$CHEt \cdot CH_2$$

(I.)
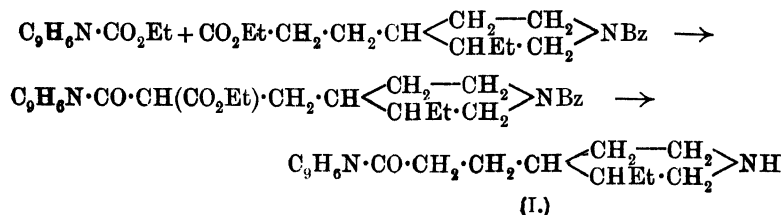
verted by known methods [60] into dihydrocinchoninone and dihydro-quininone respectively. From these ketones, dihydrocinchonine and dihydrocinchonidine on the one hand, and dihydroquinine and dihydroquinidine on the other, are produced by reduction in the same manner as quininone yields quinine and quinidine.

[58] P. Rabe and K. Kindler, loc. cit.   [59] Ibid.
[59a] Ibid., Ber., 1919, 52, [B], 1842; A., i, 78.
[60] Ann. Reports, 1918, 15, 113.

The structure of cinchonine being clear, the greater prospect of determining those of its isomerides has led to renewed investigations of their relationships to the alkaloid. Apart from cinchonidine, the stereoisomerism of which with cinchonine is represented by the formulæ (I) and (II),[61] and the ketone

$$CH_2\text{:}CH\cdot CH-CH-CH_2 \qquad CH_2\text{:}CH\cdot CH-CH-CH_2 \qquad |-CH-CH-CH_2$$

(I.)   (II.)   (III.)
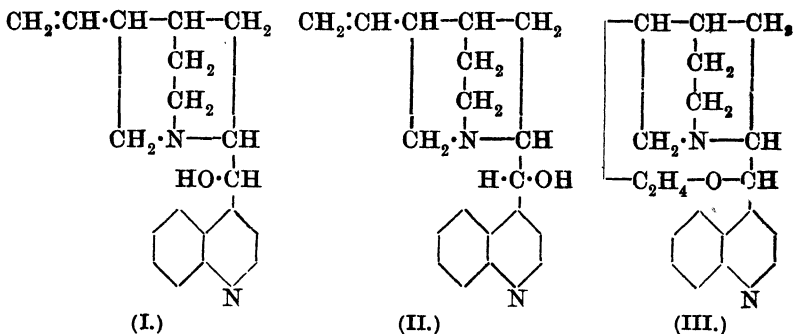
cinchotoxine, there are known *α-iso*cinchonine (cinchoniline), *β-iso*cinchonine (cinchonigine), and *apo-* or *allo*-cinchonine. These are all derived from cinchonine by the action of hydro-haloid or sulphuric acids, or by elimination of the elements of the hydrogen haloids from its hydro-haloid additive products. *apo*Cinchonine, like cinchonine itself, reacts as an unsaturated hydroxylic compound, but the others do not, and have therefore been considered to be internal ethers.[62] This has been confirmed in the case of the α-isomeride, which is stable towards dilute mineral acid, but is converted by dilute acetic or phosphoric acids into a hydroxydihydrocinchotoxine (IV), from which a hydroxydihydrocinchoninone (V) can be obtained by the general reaction previously mentioned.[63] The structure of cinchoniline is therefore repre-

(IV.)   (V.)
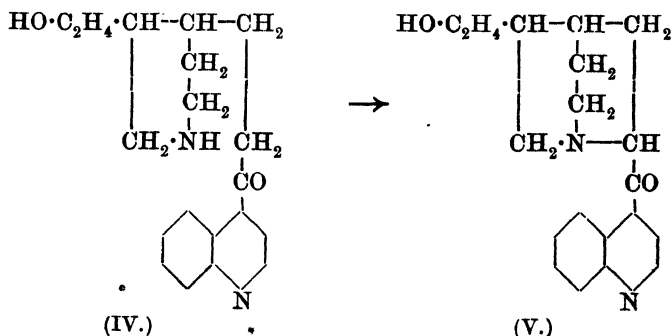
[61] P. Rabe and others, *Annalen*, 1910, **373**, 85; *A.*, 1910, i, 417.

[62] W. Koenigs, *ibid.*, 1906, **347**, 185; *A.*, 1906, i, 762.

[63] P. Rabe and B. Böttcher, *Ber.*, 1917, **50**, 127; *A.*, 1917, i, 281.

sented by the formula (III), the nature of the group $\cdot C_2H_4\cdot$ being left undetermined. On other grounds, however, this would appear to have the ethylidene structure, since α-hydroxydihydrocinchonine gives the iodoform reaction, and therefore probably contains the grouping $CH_3\cdot CH\cdot OH\cdot$.[64] This compound, which is obtained by the addition of the elements of water to cinchonine, is probably stereoisomeric with the β-compound, produced simultaneously, since both on dehydration give α- and β-isocinchonines and apocinchonine, although in relative proportions, which are not the same in each case.[65] Further, although the three isomerides of cinchonine, on treatment with hydrogen bromide, form the same hydrobromocinchonine, this is accompanied in the cases of β-isocinchonine and apocinchonine by hydrobromo-apocinchonine. Also cinchonine and α-isocinchonine give the same hydroiodocinchonine, but β isocinchonine and apocinchonine give hydroiodoapocinchonine. It is therefore concluded that α-isocinchonine is sterically related to cinchonine and β-isocinchonine to apocinchonine, the relationship of the isomerides being expressed by the formulæ: [66]

$$CH_2\!:\!CH\cdot C_{16}H_{17}N_2\!:\!CH\cdot OH \qquad CH_3\cdot CH\cdot C_{16}H_{17}N_2\!:\!CH$$

Cinchonine. Cinchonigine and cinchoniline.

$$CH_3\cdot CH\!:\!C_{16}H_{16}N_2\!:\!CH\cdot OH$$
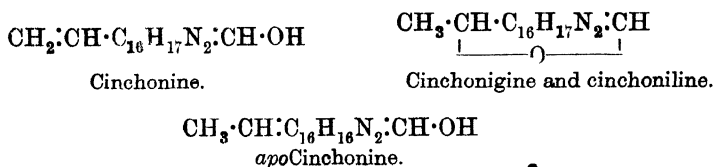
*apo*Cinchonine.

By treatment of cinchonidine with sulphuric acid, there results, besides β- and apocinchonidines, a hydroxydihydrocinchonidine, which gives the iodoform reaction, and on dehydration furnishes β- and apocinchonidines but no internal ether. This deviation from the behaviour of the hydroxydihydrocinchonines leads to the suggestion of structurally distinct formulæ for the hydroxydihydro-derivatives of cinchonidine and cinchonine.[67] These, however, need not be reproduced here, since the reader will probably find it difficult to reconcile this view with the stereoisomeric relationship of cinchonine to cinchonidine. The writer prefers to consider the difference in question as explicable by assigning the formula (I) to cinchonine, leaving the formula (II) for cinchonidine.

[64] E. Léger, *Compt. rend.*, 1918, **166**, 903; *A.*, 1918, i, 304.
[65] *Idem, ibid.*, 1919, **168**, 404; *A.*, 1919, i, 170.
[66] *Idem, ibid.*, 1918, **166**, 255, 469; *A.;* 1918, i, 182, 232.
[67] *Idem, ibid.*, 1919, **169**, 67; *A.*, 1919, i, 451.

Quinoline Dyes.

The constitution of the *iso*cyanines has been variously represented by the formulæ (I), (II), and (III):

(I.)   (II.)

(III.)   (IV.)
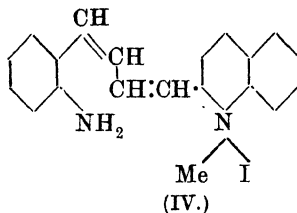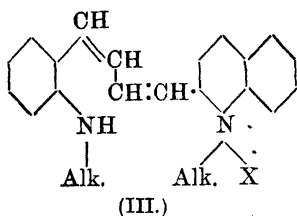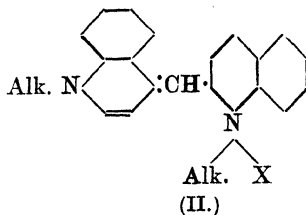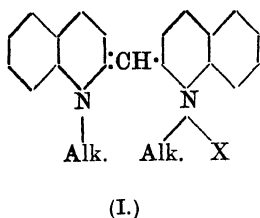
of which (II) alone explains the formation of identical products from unsubstituted quinolines and from their 4-chloro-derivatives.[68] Against (III), it has been shown [69] that the methiodide of the synthetic product (IV) resulting from the reduction of the condensation product of *o*-nitrocinnamaldehyde and quinaldine differs entirely in its properties from the *iso*cyanines. Furthermore, dimethyl*iso*cyanine acetate, on oxidation, yields 1-methyl-2-quinolone and cinchonic acid methochloride (hydrochloric acid being used in separating the two).[70] It will be seen that this result favours a formula of the type (V) rather than (II) for the

(V.)

(VI.)
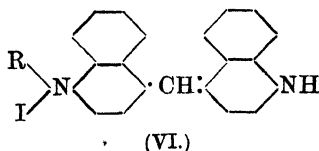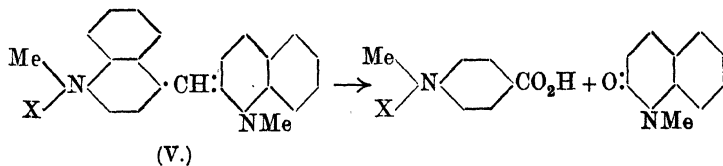
[68] A. Kaufmann and E. Vonderwahl, *Ber.*, 1912, **45**, 1404; *A.*, 1912, i, 502.
[69] W. H. Mills and P. E. Evans, *T.*, 1920, **117**, 1035.
[70] W. H. Mills and R. S. Wishart, *ibid.*, 579.

isocyanines, but it is probable that the two represent virtually tautomeric compounds. It is therefore not surprising that dyes of the isocyanine type are also obtainable [71] from the alkyl haloid additive products of sufficiently pure lepidine [72] and its homologues. From analogy. the cyanines almost certainly correspond with the formula (VI).

The constitution of pinacyanol has also been elucidated.[72a] This diethylcarbocyanine is better prepared by the action of potassium hydroxide and formaldehyde on a mixture of the ethiodides of quinoline and quinaldine than on quinaldine ethiodide alone; yet the latter is alone concerned in the reaction. By oxidation of diethylcarbocyanine bromide with dilute nitric acid, quinaldinic acid ethyl nitrate (VII) is produced, whilst by the action of potassium permanganate on the acetate, 1-ethyl-2-quinolone (VIII) is obtained. The formula (IX) is therefore adopted for pinacyanol.
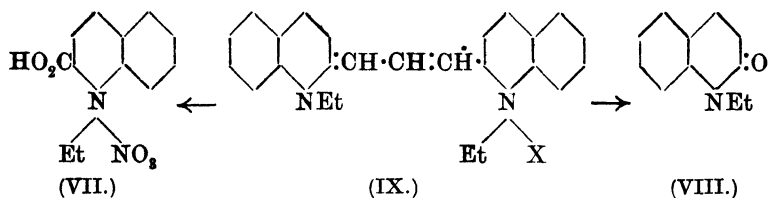
In view of the importance of these compounds in colour photography, and the fact that hitherto their manufacture had been a German monopoly, activity is being displayed in various directions in working out the details of their preparation.[73]

The Chelidonium Alkaloids.

β-Homochelidonine, an isomeride of cryptopine, resembles it in its physiological action, and in that its oxidation by mercuric acetate results in the displacement of two hydrogen atoms by an

[71] E. Q. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2389 ; *A.*, 1921, i, 53.

[72] L. A. Mikeska, *ibid.*, 2396 ; *A.*, 1921, i, 54.

[72a] W. H. Mills and (Miss) F. M. Hamer, *T.*, 1920, **117**, 1550; compare O. Fischer, *J. pr. Chem.*, 1918, [ii], **98**, 204; *A.*, 1919, i, 172 ; L. E. Wise, E. Q. Adams, J. K. Stewart, and C. H. Lund, *J. Ind. Eng. Chem.*, 1919, **11**, 460 ; *A.*, 1919, i, 416.

[73] H. Barbier, *Bull. Soc. chim.*, 1920, [iv], **27**, 427 ; *A.*, i, 568; L. E. Wise, E. Q. Adams, J. K. Stewart, and C. H. Lund, *J. Ind. Eng. Chem.*, 1919, **11**, 460 ; *A.*, 1919, i, 416 ; L. A. Mikeska, H. L. Haller, and E. Q. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 2392 ; *A.*, 1921, i, 54 ; (Sir) W. J. Pope, *J. Soc. Chem. Ind.*, 1920, **39**, 370R.

oxygen atom. It is therefore called *allo*cryptopine, and represented by the formula (II),[74] that for cryptopine being (I):

(I.)   (II.)

(III.)
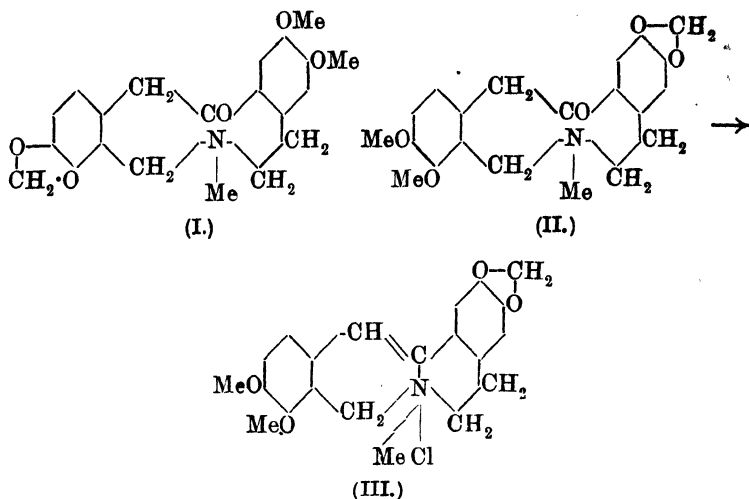
In conformity with this, *allo*cryptopine is converted by treatment with phosphoryl chloride into dihydroberberine methochloride (III), just as *iso*cryptopine chloride is obtained from cryptopine. Similarly, dihydro*allo*cryptopine (IV) gives tetrahydroberberine methochloride (V):

(IV.)

(V.)
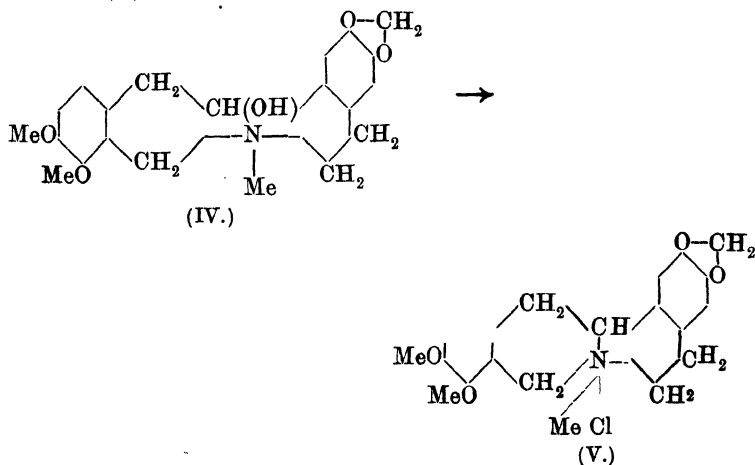
The authors of the formulæ (I and II) have each expressed some misgivings in attributing a ten-membered ring structure to natural

[74] J. Gadamer, *Arch. Pharm.*, 1919, **257**, 298; 1920, **258**, 148; *A.*, i, 75, 872.

products. It is, however, now suggested that the salts of these alkaloids, which is the form in which they occur naturally, contain two six-membered rings, and that the ten-membered ring is only produced when the bases are isolated. The changes involved are formulated as follows:
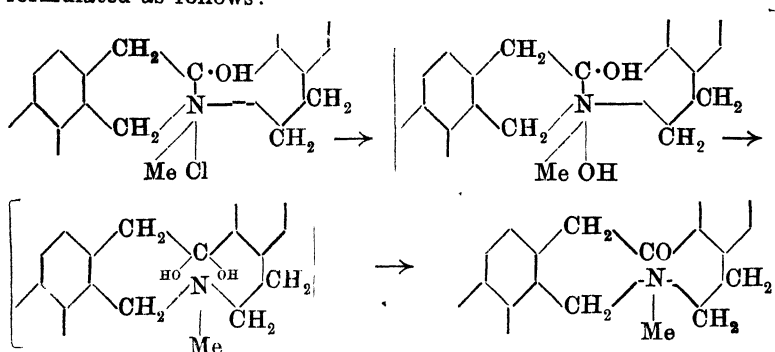
This view readily explains the fact that the bases are only gradually precipitated from solutions of their salts by alkali.

Sufficient progress has been made towards the determination of the constitution of chelidonine and α-homochelidonine to permit the deduction of provisional formulæ for these alkaloids as a working basis. They differ from *allo*cryptopine in that on oxidation with mercuric acetate, they merely lose two atoms of hydrogen. The reaction serves, however, to connect these compounds with chelerythrine, since the product from α-homochelidonine has been identified as dihydrochelerythrine.

Codeine.

A considerable advance towards the determination of the constitution of codeine and its congeners has been made by the preparation of two structurally distinct forms of tetrahydrodeoxycodeine.[75] Of these, the α-form, which had been previously obtained from deoxycodeine by means of sodium and alcohol, was considered to be a dihydro-derivative, but its formation from codeine by the following series of reactions:

$$C_{18}H_{21}O_3N \xrightarrow[\text{(Pd.)}]{H_2} C_{18}H_{23}O_3N \xrightarrow{PCl_5} C_{18}H_{22}O_2NCl \xrightarrow[\text{(electrolytic)}]{H_2}$$

Codeine. Dihydrocodeine. Chlorodihydrocodide.

$$C_{18}H_{23}O_2N \xrightarrow[\text{(Pd.)}]{H_2} C_{18}H_{25}O_2N,$$

Dihydrodeoxy- α-Tetrahydro-
codeine. deoxycodeine.
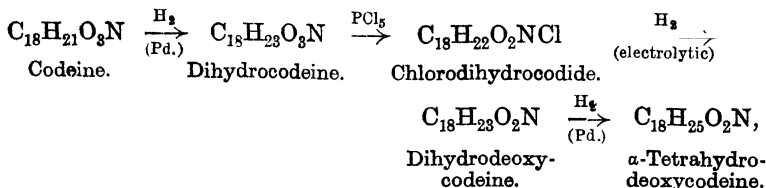
[75] M. Freund, W. W. Melber, and E. Schlesinger, *J. pr. Chem.*, 1920, [ii], **101,** 1; *A.*, i, 757.

leaves no doubt as to its composition. The absorption by deoxy-codeïne of two molecular proportions of hydrogen in the presence of palladium is equally conclusive in respect of the β-compound. Of the two formulæ current for codeine, the first (I)[76] affords no

(I.)   (II.)
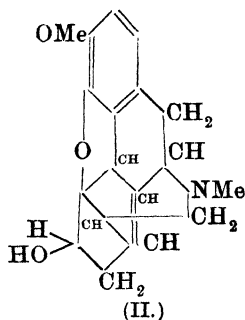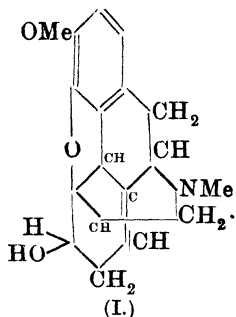
explanation of the isomerism, but according to the second (II)[77] the changes may be represented in the following way:

Deoxycodeine.
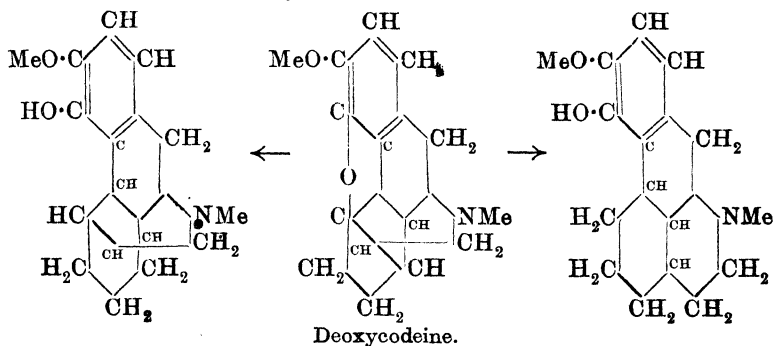
Both the tetrahydro-derivatives contain phenolic hydroxyl groups, but it is to be noted that there is at present no evidence which permits a decision as to which of the two formulæ is to be attributed to either compound.

Pyrrolidine Alkaloids.

Cuskhygrine, to which the formula (I) was assigned[78] on the grounds of its empirical composition and its oxidation to hygric acid (A), is in reality αγ-di-N-methyl-2-pyrrolidylpropan-β-one (II).[79] Its asymmetry follows from the formation of two distinct

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[76] L. Knorr and H. Hörlein, *Ber.*, 1907, **40**, 3341; *A.*, 1907, i, 789; compare J. von Braun, *Ber.*, 1914, **47**, 2312; *A.*, 1914, i, 1138.

[77] M. Freund and E. Speyer, *ibid.*, 1916, **49**, 1287; *A.*, 1916, i, 738.

[78] C. Liebermann and G. Cybulski, *ibid.*, 1895, **28**, 585; *A.*, 1895, i, 310.

[79] K. Hess and H. Fink, *ibid.*, 1920, **53**, [B], 781; *A.*, i, 497.

hydrazones, which are notable as the first examples of their kind, and are reduced by sodium ethoxide respectively to di-N-methyl-2-

$$\begin{array}{c} CH_2\!-\!CH_2 \\ CH_2 \quad CH\cdot CH_2\cdot CO\cdot CH_2\cdot CH \quad CH_2 \\ \diagdown N Me \diagup \qquad\qquad \diagdown N Me \diagup \end{array}$$

(I.)

$$\begin{array}{c} CH_2\!-\!CH_2 \quad CH_2\!-\!CH_2 \qquad\qquad CH_2\!-\!CH_2 \\ CH_2 \quad CH\cdot CH\!-\!CH \quad CH_2 \qquad CH_2 \quad CH\cdot CO_2H \\ \diagdown N Me \diagup \;\; COMe \;\; \diagdown N Me \diagup \qquad \diagdown N Me \diagup \end{array}$$
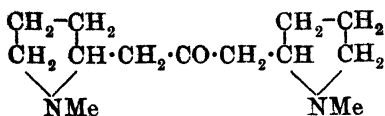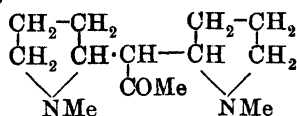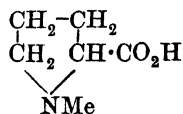
(II.) (A.)

pyrrolidylmethane (IV) and $\alpha\alpha$-di-N-methyl-2-pyrrolidylpropane (V). The alkaloid does not respond to the usual tests for the

$$\begin{array}{c} CH_2\!-\!CH_2 \quad CH_2\!-\!CH_2 \\ CH_2 \quad CH\cdot CH\cdot CH \quad CH_2 \qquad \xleftarrow{\;\alpha\;form\;} \\ \diagdown N Me \diagup \;\; Et \;\; \diagdown N Me \diagup \end{array}$$

(V.)

$$\begin{array}{c} CH_2\!-\!CH_2 \qquad\qquad\qquad CH_2\!-\!CH \\ CH_2 \quad CH\!-\!\!-\!CH\!-\!\!-\!\!-\!CH_2 \quad CH_2 \\ \diagdown N Me \diagup \;\; MeC\!:\!N\cdot NH_2 \;\; \diagdown N Me \diagup \end{array}$$

$$\xrightarrow{\;\beta\;form\;}$$

$$\begin{array}{c} CH_2\!-\!CH_2 \quad CH_2\!-\!CH_2 \\ CH_2 \quad CH\cdot CH_2\cdot CH \quad CH_2 \\ \diagdown N Me \diagup \quad \diagdown N Me \diagup \end{array}$$
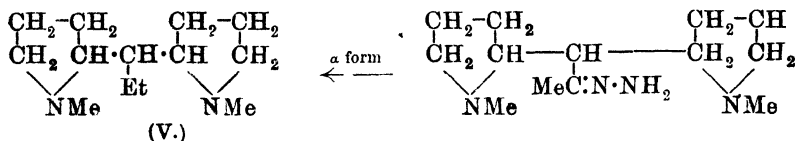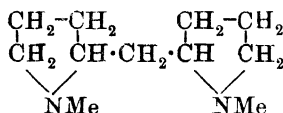
(IV.)

$\cdot CH_2\cdot CO\cdot$ grouping, but absorbs six molecular proportions of nitric oxide in the presence of sodium ethoxide. This reaction has not been utilised since its discovery,[80] but promises to be specially valuable in such cases in that it permits the rupture of the molecule by a smooth alkaline hydrolysis into simpler recognisable fragments. In the present instance there are thus obtained methylenedi*is*onitroamine, N-methyl-2-pyrrolidylacetic acid, and a mixture of unsaturated, more or less completely demethylated, bases of the type (VI), which by reduction and re-methylation give the above di-N-methyl-2-pyrrolidylmethane as sole product:

$$\begin{array}{c} CH_2\!-\!CH_2 \quad N_2O_2H \quad CH_2\!-\!CH_2 \\ CH_2 \quad CH\!-\!C\!-\!\!-\!\!-\!\!-\!\!-\!CH \quad CH_2 \qquad \longrightarrow \\ \diagdown N Me \diagup \;\; CO \;\; \diagdown N Me \diagup \\ \qquad CH(N_2O_2H)_2 \end{array}$$

$$CH_2(N_2O_2H)_2 \;+\; \begin{array}{c} CH_2\!-\!CH_2 \\ CH_2 \quad CH\cdot CH_2\cdot CO_2H \\ \diagdown N Me \diagup \end{array} \;+\; \begin{array}{c} CH_2\!-\!CH_2 \quad CH_2\!-\!CH_2 \\ CH_2 \quad CH\cdot CH\!:\!C \quad CH_2 \\ \diagdown N Me \diagup \quad \diagdown N Me \diagup \end{array}$$
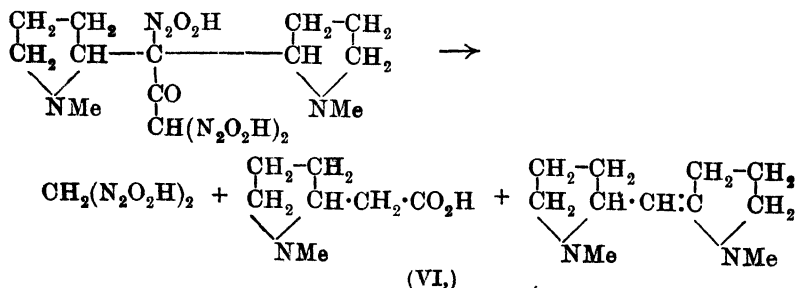
(VI,)

[80] W. Traube, *Annalen*, 1898, **300**, 81; *A.*, 1898, i, 349.

By the action of potassium hydroxide, cuskhygrine is converted into hygrine. It is suggested that a similar reaction may occur in nature, and further that the carboxyl group of ecgonine may represent an oxidised pyrrolidine nucleus of cuskhygrine.

A reaction [81] which may well render the synthesis of cocaine and related compounds a commercial possibility consists in the application of the Dieckmann reaction to diethyl N-methyl-2 : 5-pyrrolidyldiacetate, which is obtained by the action of methylamine on diethyl succinyldiacetate. The condensation product thus obtained is then reduced in glacial acetic acid solution by hydrogen in the presence of platinum :

$$\begin{array}{c} CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \\ CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \end{array} + CH_3{\cdot}NH_2 \rightarrow \begin{array}{c} CH{:}C{\cdot}CH_2{\cdot}CO_2Et \\ | \quad NMe \\ CH{:}C{\cdot}CH_2{\cdot}CO_2Et \end{array} \rightarrow$$

$$\begin{array}{c} CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO_2Et \\ | \quad NMe \\ CH_2{\cdot}CH{\cdot}CH_2{\cdot}CO_2Et \end{array} \rightarrow \begin{array}{c} CH_2{\cdot}CH{-}CH{\cdot}CO_2Et \\ | \quad NMe \quad CO \\ CH_2{\cdot}CH{-}CH_2 \end{array}$$
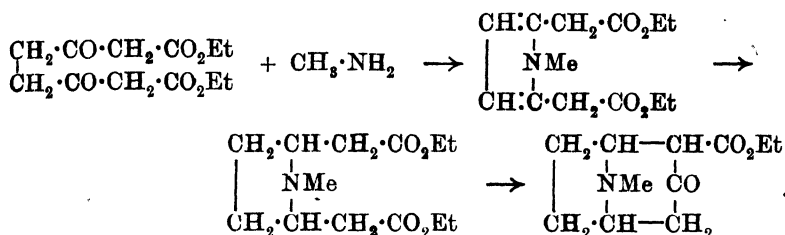
The ethyl tropinonecarboxylate produced may be reduced electrolytically or by sodium amalgam to the ethyl ester of r-ecgonine.

The constitution of scopolamine and scopoline has now been determined. As scopoline was known to be an internal ether, from which hydroscopoline (1 : 2-dihydroxytropan),[82] A, was

$$\begin{array}{c} \overset{4}{C}H_2{-}\overset{5}{C}H_2{-}\overset{6}{C}H_2 \\ | \qquad\qquad | \\ {}_3CH{\cdot}NMe{\cdot}CH\,_7 \\ | \qquad\qquad | \\ \underset{2}{C}H(OH){-}\underset{1}{C}H{\cdot}OH \end{array}$$
$$A.$$
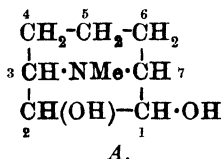
derived by rupture of the etheric linkage [83] through the addition of two hydrogen atoms, it only remained to determine which of the other atoms of the molecule is involved in the oxide ring. The remarkable results of the degradation of scopoline by exhaustive methylation permit a decision on this point.[84] Although the distillation of scopoline methohydroxide under ordinary pressure results in profound decomposition,[85] under diminished pressure satisfactory

[81] R. Willstätter, D.R.-P. 302401; A., i, 680.

[82] Ann. Reports, 1918, 15, 112.

[83] E. Schmidt, Apoth. Zeit., 1902, 17, 592; A., 1903, i, 51.

[84] K. Hess, Ber., 1919, 52, [B], 1947; A., i, 81.

[85] W. Luboldt, Arch. Pharm., 1898, 236, 26; A., 1898, i, 499; E. Schmidt, Arch. Pharm., 1905, 243, 566; A., 1906, i, 103.

results are obtained. In place of the expected product, however, an isomeric, doubly unsaturated tertiary base, ψ-demethylscopoline (II), is obtained. The crucial result follows from the attempt to degrade this compound by exhaustive methylation, and may be considered in the following manner, which differs somewhat from that in the original paper. The product has a molecular formula greater by one methylene group than that of ψ-demethylscopoline, due to the presence of a methoxy-group. The double bonds present have no influence on the result, because the product gives a tetra-hydro-derivative (IV), which is identical with that similarly obtained from tetrahydro-ψ-demethylscopoline (V). Although a free hydroxyl group is no longer present, it cannot be assumed that direct methylation of the hydroxyl group in ψ-demethylscopoline has occurred under such conditions. Hence the oxygen atom of the etheric linkage must have been methylated as the result of a profound molecular rearrangement, the product therefore being called O-methyliso-ψ-demethylscopoline (III). Such a change, how-ever, can only be adequately explained by assuming that the dimethylamino-group of ψ-demethylscopoline is attached to one of the carbon atoms carrying the etheric linkage, which is destroyed so easily. This atom must therefore be 3- or 7- of the tropine ring. Assuming that the other carbon atom involved in the ether struc-ture is that in position 2, the former is excluded because it would involve the initial formation of a double bond in the original degradation of N-methylscopoline either in the 1 : 7- or the 6 : 7-posi-tions. Of these, the first would represent the formation of the enolic form of a ketone, which is not observed, and the second supplies no explanation of the instability of the initial product and its rearrangement to a doubly unsaturated compound. This, how-ever, is at once forthcoming on the assumption that the dimethyl-amino-group of ψ-demethylscopoline is attached to the 7-carbon atom, as will be seen from the scheme on p. 129. The formula for scopoline is therefore represented by (I), whilst that for scopolamine is (VI).

One of the two quaternary carbon atoms is seen to be responsible for each of the rearrangements. It is noteworthy that both O-methyliso-ψ-demethylscopoline and its tetrahydro-derivative are recovered unchanged when the attempt is made to degrade them further by exhaustive methylation.

The results of this investigation are an excellent illustration of the valuable information as to the factors which modify the stability of cyclic compounds to be derived from a study of natural

$$\begin{array}{c} \text{CH}_2\text{·CH}_2\text{·CH}_2 \\ | \qquad\qquad | \\ \text{CH·NMe·C} \\ |\diagdown^{\text{O}}\diagup| \\ \text{CH}\!-\!\!-\!\!-\!\text{CH·OH} \\ \text{(I.)} \end{array} \rightarrow \left[\begin{array}{c} \text{CH}_2\text{·CH}_2\text{·CH}_2 \\ | \qquad\qquad | \\ \text{CH} \qquad \text{C·NMe}_2 \\ \|\diagdown^{\text{O}}\diagup| \\ \text{C}\!-\!\!-\!\!-\!\text{CH·OH} \end{array}\right] \rightarrow \begin{array}{c} \text{CH}_2\text{:CH·CH}_2 \\ | \qquad\qquad | \\ \text{CH}_2 \qquad \text{C·NMe}_2\!-\!\! \\ \|\diagdown^{\text{O}}\diagup| \\ \text{C}\!-\!\!-\!\!-\!\text{CH·OH} \\ \text{(II.)} \end{array}$$

$$\rightarrow \left[\begin{array}{c} \text{CH}_2\text{·CH·CH}_2 \\ | \qquad\qquad | \\ \text{CH}_2 \qquad \text{C(OH)·NMe}_2 \\ \| \qquad\qquad | \\ \text{C(OMe)}\!-\!\text{CH·OH} \end{array}\right] \xrightarrow{} \begin{array}{c} \text{CH}_2\text{:CH·CH}_2 \\ | \qquad\qquad | \\ \text{CH}_2 \qquad \text{C·NMe}_2 \\ \| \qquad\qquad |\!\!>\!\!\text{O} \\ \text{C(OMe)}\!-\!\text{CH} \\ \text{(III.)} \end{array} \xrightarrow{} \begin{array}{c} \text{CH}_3\text{·CH}_2\text{·CH}_2 \\ | \qquad\qquad | \\ \text{CH}_3 \qquad \text{C·NMe}_2 \\ | \qquad\qquad |\!\!>\!\!\text{O} \\ \text{CH(OMe)·CH} \\ \text{(IV.)} \end{array}$$

$$\Big\uparrow$$

$$\begin{array}{c} \text{CH}_2\text{·CH}_2\text{·CH}_2 \\ | \qquad\qquad | \\ \text{CH·NMe·C} \\ |\diagup^{\text{O}}\diagdown| \\ \text{CH}\!-\!\!-\!\!-\!\text{CH·O·CO·CHPh·CH}_2\text{·OH} \\ \text{(VI.)} \end{array} \qquad\qquad \begin{array}{c} \text{CH}_3\text{·CH}_2\text{·CH}_2 \\ | \qquad\qquad | \\ \text{CH}_3 \qquad \text{C·NMe}_2\!\leftarrow\!\! \\ |\diagup^{\text{O}}\diagdown| \\ \text{CH}\!-\!\!-\!\!-\!\text{CH·OH} \\ \text{(V.)} \end{array}$$
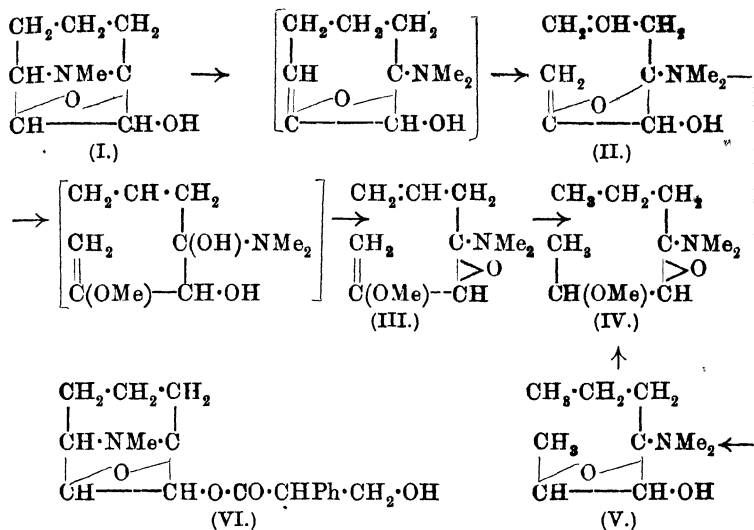
products—made up as they often are of structures not obtainable in the laboratory.

J. KENNER.

ANALYTICAL CHEMISTRY.

THE contributions to this branch of chemistry have been of a much more varied character during the past year than has been the case during the preceding five years. America has continued to show the greatest activity in this respect, whilst the conditions in this and other countries more seriously affected by the war have not yet become normal.

The main material difficulties in the way of analytical work have been the lack of an adequate supply of suitable glass apparatus and the continued shortage of platinum. Further devices have, therefore, been proposed to obviate the use of that metal.[1] For example, it has been shown that for certain quantitative estimations, such as the analysis of chrome iron ore, platinum basins may be replaced by lead basins,[2] whilst iron basins are suitable for sulphide fusions.[3] An efficient substitute for platinum wire for flame tests may be prepared from a strip of rolled filter paper,[4] or from the "lead" of a black-lead pencil.[5]

Physical Methods.

A new form of viscosimeter of the capillary type has been devised. The oil or other liquid is forced up into the tube by the compression of a bulb, the temperature brought to a definite point by means of a thermostatic jacket, and the time required for the liquid to fall between given points is noted. The absolute vicosity is then calculated by means of the formula: $\eta = Kdt$, where K represents a constant of the apparatus, d the specific gravity of the liquid, and t the time in seconds.[6]

The errors associated with the falling sphere type of viscosimeter have been taken into consideration in a new instrument,

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[1] Compare *Ann. Reports*, 1918, **15**, 118 ; 1919, **16**, 127.

[2] C. Hütter, *Zeitsch. angew. Chem.*, 1919, **32**, 380 ; *A.*, ii, 189.

[3] H. Sertz, *ibid.*, 1920, **33**, i, 156.

[4] A. Ehringhaus, *Centr. Min.*, 1919, 192 ; *A.*, ii, 263.

[5] C. C. Kiplinger, *J. Ind. Eng. Chem.*, 1920, **12**, 500 ; *A.*, ii, 381.

[6] G. Baume and H. Vigneron, *Ann. Chim. anal.*, 1919, [ii], **1**, 379 ; *A.*, ii, 92.

in which the steel ball is delivered into the centre of the tube, and corrections for the wall and end effects are applied, the result being calculated into absolute viscosity by means of a modification of Stokes' equation.[7]

Fischer's viscosimeter, which is particularly suitable for very viscid liquids, consists essentially of an inner tube surrounded by a water jacket, resembling a vertical Liebig's condenser, through which water at a definite temperature is run. The viscosity is measured by the time required by a metal ball to fall between two points on the inner tube.[8]

A viscosimeter may be used for determining the density of a liquid of which only a few c.c. are available,[9] the calculation being made by a combination of the formulæ of Ostwald-Poiseuille and of Scarpa.[10]

The determination of the surface tension affords a means of identifying minute quantities of organic liquids. A capillary tube containing a short column of the liquid is turned until the lower meniscus of the latter changes to a plane surface, and the angular deviation of the tube from the vertical position is then read on a quadrant scale. The surface tension, T, is calculated by means of the usual formula: $T = d \times h \times r \times 980/2$ dynes per sq. cm.[11]

For estimating the acidity of liquids, the use of surface-active indicators, as originally suggested by Traube and Somogyi,[12] is often more convenient than the use of colour indicators.[13] By using salts of alkaline nature, such as eucupine dihydrochloride, it is possible to titrate highly dissociated acids in the presence of a primary phosphate,[14] whilst the relative alkalinity of the carbonates and hydrogen carbonates of potassium, sodium, calcium, and magnesium may be determined in an analogous manner.[15]

A study of the soap-bubble method of determining the ignition temperature of gaseous mixtures[16] has shown that, even after careful standardisation of the coils, size of bubble, and other details, the results cannot be depended on, even for comparative purposes.[17]

[7] W. H. Gibson and (Miss) L. M. Jacobs, *T.*, 1920, **117**, 473.

[8] *Chem. Zeit.*, 1920, **44**, 622.

[9] W. Block, *Zeitsch. angew. Chem.*, 1920, **33**, 198 ; *A.*, ii, 590.

[10] *Gazzetta*, 1910, **40**, ii, 261 ; *A.*, 1911, ii, 17.

[11] C. C. Kiplinger, *J. Amer. Chem. Soc.*, 1920, **42**, 472 ; *A.*, ii, 291.

[12] *Int. Zeitsch phys.-chem. Biol.*, 1914, **1**, 479 ; *A.*, 1915, ii, 101.

[13] W. Windisch and W. Dietrich, *Biochem. Zeitsch.*, 1919, **100**, 130 ; *A.*, ii, 48.

[14] *Ibid.*, 135 ; *A.*, ii, 706.   [15] *Ibid.*, **101**, 82 ; *A.*, ii, 707.

[16] J. W. McDavid, *T.*, 1917, **111**, 1003.

[17] A. G. White and T. W. Price, *ibid.*, 1919, **115**, 1248.

The melting-point curves obtained with binary and ternary mixtures of nitronaphthalenes may be used in the analysis of the industrial products of nitration. The simultaneous presence of mono- and tri-nitronaphthalene is indicated by points of arrest in the cooling curves.[18] Even when the melting point of the pure substance is not known, the freezing-point curve affords an indication of the amount of impurity present.[19]

A new physico-chemical method of examining double salts has been based on the measurement of the temperature produced on mixing the solutions with a constant liquid, such as phenol. When a double salt is in solution, there is a variable difference between the observed and calculated results.[20]

Turning to optical methods, it has been shown that the ion content of an aqueous solution of salts may be calculated from the refractive indices of the liquid before and after precipitation of one of the component salts.[21]

Small amounts of lead in copper may be estimated spectroscopically,[22] the time required for the bright lead line ($405\cdot8\ \mu\mu$) under constant conditions being noted. Another application of spectrophotometry is in the analysis of colourless organic compounds, which for this purpose are converted into coloured compounds.[23]

Reference may also be made to a new form of nephelometer[24] and to a photographic turbidimeter, in which one beam of light is passed through the column of suspended substance and a second beam of equal intensity through standardised glass disks.[25] In the nephelometric estimation of chlorides, the intensity of the opalescence of the silver chloride suspension is increased and rendered more constant by heating the liquid to 40° after the precipitation.[26] The nephelometric values of cholesterol and the higher fatty acids have been shown to be affected by hydrolysis and by the presence of other substances, which, by themselves, do not produce turbidity.[27]

The comparison of the fluorescence produced by ultra-violet rays

[18] P. Pascal, *Bull. Soc. chim.*, 1920, [iv], **27**, 388 ; *A.*, ii, 514.

[19] W. P. White, *J. Physical Chem.*, 1920, **24**, 393 ; *A.*, ii, 529.

[20] R. Dubrisay, *Compt. rend.*, 1920, **170**, 1582 ; *A.*, ii, 508.

[21] M. de Crinis, *Zeitsch. physiol. Chem.*, 1920, **110**, 254 ; *A.*, ii, 700.

[22] C. W. Hill and G. P. Luckey, *Trans. Amer. Electrochem. Soc.*, 1917, **32**, 335 ; *A.*, ii, 193.

[23] W. E. Mathewson, *J. Amer. Chem. Soc.*, 1920, **42**, 1277 ; *A.*, ii, 566.

[24] C. Chéneveau and R. Audubert, *Compt. rend.*, 1920, **170**, 728 ; *A.*, ii, 327.

[25] W. G. Bowers and J. Moyer, *J. Biol. Chem.*, 1920, **42**, 191 ; *A.*, ii, 444.

[26] A. B. Lamb, P. W. Carleton, and W. B. Meldrum, *J. Amer. Chem. Soc.*, 1920, **42**, 251 ; *A.*, ii, 383.

[27] F. A. Csonka, *J. Biol. Chem.*, 1920, **41**, 243 ; *A.*, ii, 272.

on substances in the cylinders of a nephelometer affords a new means of quantitative analysis.[28]

A physical method of identifying and determining the purity of acids has been based on the observation of their dissociation constant, which may be determined, for example, by comparing the change of colour of the same indicator in the solution and in a standard solution of known hydrogen-ion concentration.[29] A simple method of determining the ion concentration of ultra-filtrates and other solutions free from proteins is to add an ion forming a sparingly soluble salt with the ion in question, and to note the limit of solubility, as indicated by the formation of a milky turbidity. In the case of calcium, the method gives results accurate within 2 to 3 milligrams per litre.[30]

A method of analysis by fractional distillation under a constant reduced pressure is useful for the separation of substances having boiling points which are close together. The fractionation is continued until the final fractions show, not only identical boiling points, but also agree in their other physical properties, such as density, refractive index, and viscosity.[31]

Gas Analysis.

Various instruments for the automatic analysis of gases or for the detection of an individual constituent have been described. The katharometer, which is intended for the estimation of small quantities of hydrogen in air, is based on the change in the electrical resistance of a platinum helix through the increase in temperature caused by surface combustion of the hydrogen.[32] An analogous principle has been utilised in the estimation of carbon monoxide in air.[33]

The thermal conductivity method can only be applied quantitatively when the probable identity and amounts of constituents likely to be present in a gaseous mixture are known, but under such conditions it gives good results in many cases.[34]

[28] L. J. Desha, J. Amer. Chem. Soc., 1920, 42, 1350 ; A., ii, 552.

[29] I. M. Kolthoff, Pharm. Weekblad, 1920, 57, 514 ; A., ii, 628.

[30] R. Brinkman and (Miss) E. van Dam, Proc. K. Akad. Wetensch. Amsterdam, 1920, 22, 762 ; A., ii, 510.

[31] C. Moureu, C. Dufraisse, and P. Robin, Bull. Soc. chim., 1920, [iv], 27, 523 ; A., ii, 562.

[32] H. A. Daynes and G. A. Shakespear, Proc. Roy. Soc., 1920, 97, [A], 273 ; A., ii, 503.

[33] A. B. Lamb and A. T. Larson, J. Amer. Chem. Soc., 1919, 41, 1908 ; A., ii, 126.

[34] E. R. Weaver and P. E. Palmer, J. Ind. Eng. Chem., 1920, 12, 894 ; A., ii, 701.

Another instrument which may be used for the estimation of small amounts of hydrogen or helium in air is the interferometer, which measures the difference in the refractivity of two gases.[35]

A weighing burette for use in gas analysis has been devised, the weight of the gas and alterations in volume caused by the absorption of the constituents being determined by weighing the quantity of mercury which is removed from, or introduced into, the burette.[36] Improved modifications of Orsat's apparatus have also been described.[37, 38]

A source of error in the analysis of gases by fractional combustion with copper oxide is the dissociation of the latter, with the liberation of oxygen. This may be obviated by subsequently passing the nitrogen repeatedly over the oxide at a moderate red heat.[39]

The use of an ammoniacal copper solution has several advantages over alkaline pyrogallol as an absorbent for the estimation of oxygen. If the usual ammonium carbonate solution be replaced by saturated ammonium chloride solution, the gas will be free from carbon dioxide derived from the reagent.[40] On the other hand, when freshly prepared, it may impart traces of ammonia to the gas, and cannot be used in the case of gases containing carbon monoxide or acetylene.[41]

For the estimation of the latter, good results may be obtained, under certain conditions, by the use of ammoniacal cuprous chloride solution as absorption reagent, the solution being then acidified with acetic acid, and the cuprous acetylide separated and estimated.[42] Another suitable reagent for the absorption of acetylene is a solution of mercuric cyanide in sodium hydroxide solution. This effects its separation from ethylene and benzene vapour. For the absorption of ethylene in the presence of benzene, a solution of mercuric nitrate in dilute nitric acid saturated with sodium nitrate may be used.[43] Ilosvay's reagent[44]

[35] J. C. McLennan and R. T. Elworthy, *Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 19 ; *A.*, ii, 508.

[36] E. R. Weaver and P. G. Ledig, *J. Amer. Chem. Soc.*, 1920, **42**, 1177 ; *A.*, ii, 502.

[37] T. B. Smith, *Gas World*, 1919, **71**, 379 ; *A.*, ii, 263.

[38] G. W. Jones and F. R. Neumeister, *Chem. and Met. Eng.*, 1919, **21**, 734 ; *A.*, ii, 119.

[39] E. Ott, *J. Gasbeleucht.*, 1919, **62**, 89 ; *A.*, ii, 52.

[40] W. Haehnel and M. Mugdan, *Zeitsch. angew. Chem.*, 1920, **33**, 35 ; *A.*, ii, 191.

[41] W. L. Badger, *J. Ind. Eng. Chem.*, 1920, **12**, 161 ; *A.*, ii, 264.

[42] J. A. Muller, *Bull. Soc. chim.*, 1920, [iv], **27**, 69 ; *A.*, ii, 198.

[43] W. D. Treadwell and F. A. Tauber, *Helv. Chim. Acta*, 1919, **2**, 601 ; *A.*, ii, 61.   [44] *Ber.*, 1899, **32**, 2697 ; *A.*, 1900, ii, 52.

removes acetylene quantitatively from coal gas or air, and good results may be obtained by igniting the precipitate with nitric acid and weighing the copper oxide. Hydrogen sulphide must not be present, and in the case of air containing not more than 0·04 per cent. of acetylene, about 5 per cent. of carbon dioxide must be added to prevent oxidation.[45] Methods depending on the reaction of acetylene with silver nitrate, and titration of the liberated nitric acid, are inaccurate, owing to the impossibility of controlling the conditions of the reaction. Good results may be obtained, however, by causing the copper acetylide, separated with Ilosvay's reagent, to react with a sulphuric acid solution of ferric sulphate, and titrating the resulting ferrous sulphate.[46]

A satisfactory reagent for the absorption of carbon monoxide may be prepared by reducing cupric chloride in acid solution by means of stannous chloride. The presence of a slight excess of the latter prevents oxidation by the air, and the reagent may be renewed by expelling the absorbed gas at 60—70°.[47]

A method of detecting and estimating traces of $\beta\beta'$-dichlorodiethyl sulphide (mustard gas) in air has been based on its reducing action on a solution of selenious acid in sulphuric acid, the amount of the orange-red suspension of selenium being estimated by nephelometric comparison with standard suspensions. The selenious reagent also reacts in the same way with arsines and other toxic gases.[48]

Agricultural Analysis.

There has been a considerable amount of investigation as to the most suitable methods of estimating the acidity and the lime requirement of soils. Extraction of an acid soil with potassium nitrate solution, as in the method of Hopkins and Pettit, has been shown to give the same results as extraction with equivalent solutions of potassium chloride, sodium nitrate, sodium chloride, or calcium chloride, whilst variations in the temperature between 25° and 90° do not affect the acidity of the extract. There is little, if any, exchange of acid radicles during the extraction.[49]

[45] H. Arnold, E. Möllney, and F. Zimmermann, *Ber.*, 1920, **53**, [B], 1034 ; *A.*, ii, 513.

[46] R. Willstätter and E. Maschmann, *ibid.*, 939 ; *A.*, ii, 514.

[47] F. C. Krauskopf and L. H. Purdy, *J. Ind. Eng. Chem.*, 1920, **12**, 158 ; *A.*, ii, 267.

[48] M. Yablik, G. St. J. Perrott, and N. H. Furman, *J. Amer. Chem. Soc.*, 1920, **42**, 266 ; *A.*, ii, 272.

[49] H. G. Knight, *J. Ind. Eng. Chem.*, 1920, **12**, 340 ; *A.*, i, 468.

For estimating the lime requirement, the vacuum method[50] gives trustworthy results agreeing with those obtained by the use of a hydrogen electrode after a specified period of shaking, whilst in the case of limed soils the reduction in the acidity is best ascertained by the hydrogen electrode method or the Hopkins method.[51] The method of estimating the acidity or alkalinity of a soil in terms of P_H[52] has been adapted for use in field tests, and a table has been constructed showing the reactions of the soil corresponding with the colour changes of a series of indicators, each of which overlaps the next in the scale.[53]

For the estimation of the total calcium in soils, a method has been devised in which the precipitation with ammonia, and consequent occlusion of calcium in the precipitate, are eliminated. The precipitation is effected by adding solid ammonium oxalate to the boiling solution, which has been rendered first just alkaline with ammonia, and then just acid with hydrochloric acid, and manganese is subsequently separated from the precipitated oxalate.[54] In an investigation of ten different methods of estimating calcium in calcite, the most accurate results were obtained by precipitation as calcium oxalate and weighing as calcium oxide, by precipitation as oxalate from a slightly acid solution, and by the residual titration method.[55]

The small amounts of manganese in plant ashes and similar products can only be estimated colorimetrically. Of the different methods suggested, only that of Marshall[56] has been found to give trustworthy results.[57] In that method, the manganese is oxidised to permanganate by means of potassium persulphate. The influence of various factors on the estimation of chlorides in soil has been studied, and it has been shown that Volhard's method gives more accurate and concordant results than Mohr's method.[58]

For estimating carbonates in limestones, marl, and soil, the method of Van Slyke[59] is the most suitable for substances poor in

[50] J. W. Ames and C. J. Schollenberger, *J. Ind. Eng. Chem.*, 1916, **8**, 243; *A.*, 1916, i, 459.

[51] H. G. Knight, *ibid.*, 1920, **12**, 457, 559; *A.*, i, 587; ii, 557.

[52] E. T. Wherry, *J. Washington Acad. Sci.*, 1919, **9**, 305; *A.*, 1919, i, 428.

[53] *Ibid.*, 1920, **10**, 217; *A.*, ii, 400.

[54] O. M. Shedd, *Soil Sci.*, 1920, **10**, 1; *A.*, ii, 636.

[55] G. E. Ewe, *Chem. News*, 1920, **121**, 53; *A.*, ii, 557.

[56] *Ibid.*, 1901, **83**, 76; *A.*, 1901, ii, 350.

[57] D. H. Wester, *Rec. trav. chim.*, 1920, **39**, 414; *A.*, ii, 451.

[58] C. T. Hirst and J. E. Greaves, *Soil Sci.*, 1920, **9**, 41; *A.*, ii, 384.

[59] *J. Biol. Chem.*, 1918, **36**, 351; *A.*, 1919, ii, 78; compare *Ann. Reports*, 1919, **16**, 142.

magnesium carbonate, whilst in other cases Van Slyke's gasometric method [60] gives more accurate results.[61]

A method for the approximate estimation of phytin in plant extracts has been based on its precipitation in the presence of inorganic phosphates by an acetic acid solution of copper acetate of definite concentration, but the amounts of phytin precipitated vary with the nature of the plant.[62]

Organic Analysis.

Qualitative.—Formaldehyde gives colorations, which are not always distinctive of the aldehyde, with certain aromatic compounds, such as pyrogallol, β-naphthol, and salicylic acid, and these chromatic reactions may sometimes be used as tests of identity.[63] Another reagent which gives distinctive colorations with polyhydroxyphenols and other compounds of a phenolic character is sodium *p*-toluenedisulphochloroamide in neutral or alkaline solution, but the tests must be made under definite conditions as to the proportions of reacting substances and the temperature.[64]

Most of the tests for methyl alcohol are based on its conversion into formaldehyde, which is then identified either by chromatic reactions or by the formation of crystalline derivatives. These methods have been critically examined and their relative trustworthiness determined. Of the direct tests, all of which require a considerable proportion of methyl alcohol, that of Vivario,[65] in which the methyl alcohol is converted into potassium cyanide, gives very good results.[66]

A test to distinguish between methyl and ethyl alcohols has been based on the solubility of crystallised copper sulphate in the former,[67] but is untrustworthy in the case of mixtures of the dilute alcohols.[68] Lieben's reaction for iodoform has been modified so as to afford a sensitive test for traces of ethyl alcohol.[69]

A specific reaction for acetoacetic acid and its esters has been

[60] *J. Biol. Chem.*, 1917, **30**, 347 ; *A.*, 1917, ii, 422.
[61] C. S. Robinson, *Soil Sci.*, 1920, **10**, 41 ; *A.*, ii, 635.
[62] A. Rippel, *Biochem. Zeitsch.*, 1920, **103**, 163 ; *A.*, ii, 518.
[63] A. Rossi, *Boll. Chim. farm.*, 1919, **58**, 265 ; *A.*, ii, 63.
[64] A. Berthelot and M. Michel, *Bull. Sci. Pharmacol.*, 1919, **26**, 401 ; *A.*, ii, 336.
[65] *J. Pharm. Chim.*, 1914, [vii], **10**, 145 ; *A.*, 1914, ii, 780.
[66] A. O. Gettler, *J. Biol. Chem.*, 1920, **42**, 311 ; *A.*, ii, 562.
[67] Pannwitz, *Pharm. Zentr.-h.*, 1919, **60**, 441 ; *A.*, ii, 62.
[68] T. Sabalitschka, *ibid.*, 1920, **61**, 78 ; *A.*, ii, 271.
[69] R. Kunz, *Zeitsch. anal. Chem.*, 1920, **59**, 302 ; *A.*, ii, 711.

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based on its condensation in hydrochloric acid solution to form β-methylumbelliferone, which in alkaline solution shows an intense blue fluorescence.[70]

From a study of various reactions for the identification of traces of hydrocyanic acid, the conclusion has been drawn that the ferrocyanide test is the most characteristic.[71] The Prussian-blue test gives a reaction at a dilution of about $1:17 \times 10^4$ with hydrocyanic acid, whilst the Schönbein test, which is not distinctive, gives a reaction at $1:43 \times 10^6$ in the light and at 1.55×10^6 in the dark.[72] A test paper impregnated with a solution of o-tolidine, copper acetate, and dilute acetic acid is capable of detecting one part of hydrocyanic acid in two million parts of air.[73]

In the colour reaction with manganese salts for oxalates,[74] sufficient oxidation is produced by agitating the hot solution with a little alkali hydroxide.[75] Oxalic acid may be distinguished from tartaric and lactic acids by giving a violet coloration when heated with sulphuric acid and resorcinol.[76] If the test be applied as a zone reaction, a blue ring is formed at the junction of the liquids.[77]

A biochemical method of detecting dextrose in the presence of other sugars, such as mannose, lævulose, or arabinose, has been based on its conversion, in 70 per cent. methyl alcohol solution, by emulsin into β-methylglucoside, which may be identified in crystalline form.[78] Of various tests recommended for the detection of dextrose in urine, Fehling's test is the most sensitive, being capable of detecting 0.00125 per cent.[79] Traces of acetylmethylcarbinol formed in the butylene-glycollic fermentation of sugars may be identified by oxidising the carbinol to diacetyl, which is then distilled, and identified by precipitation as nickel dimethylglyoxime.[80]

A very sensitive test for benzoic acid or for substances such as cocaine, which contain a benzoyl group, or which, like atropine, yield benzoic acid on oxidation, has been based on the diazotisation of the aminobenzoic acids produced on nitration and reduc-

[70] V. Arreguine and E. D. Garcia, *Ann. Chim. anal.*, 1920, [ii], **2**, 36 ; *A.*, ii, 273.　　　　　　　　　　　　　[71] L. Chelle, *ibid.*, 21 ; *A.*, ii, 202.

[72] J. B. Ekeley and I. C. Macy, *Proc. Colorado Sci. Soc.*, 1919, **11**, 269 ; *A.*, ii, 202.

[73] J. Moir, *J. S. African Assoc. Anal. Chem.*, 1920, **3**, 16 ; *A.*, ii, 715.

[74] V. Macri, *Boll. chim. farm.*, 1917, **56**, 377 ; *A.*, 1917, ii, 511.

[75] H. Caron and D. Raquet, *Ann. Chim. anal.*, 1919, [ii], **1**, 205 ; *A.*, 1919, ii, 438.

[76] K. Brauer, *Chem. Zeit.*, 1920, **44**, 494 ; *A.*, ii, 517.

[77] L. H. Chernoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1784 ; *A.*, ii, 712.

[78] E. Bourquelot and M. Bridel, *Compt. rend.*, 1920, **170**, 631 ; *A.*, ii, 337.

[79] G. E. Ewe, *Amer. J. Pharm.*, 1919, **91**, 717 ; *A.*, ii, 132.

[80] M. Lemoigne, *Compt. rend.*, 1920, **170**, 131 ; *A.*, ii, 198.

tion, and the formation of an orange-red precipitate on treating the diazo-compounds with an ammoniacal solution of β-naphthol.[81]

The behaviour of guaiacol with an oxydase affords a means of distinguishing it from creosote, the former giving a yellow coloration immediately, whilst the latter is colourless at first and then shows a slight violet tint.[82]

A new colour reaction for quinine, which takes place on the addition of pyridine in the presence of chlorine water, distinguishes the alkaloid from quinidine and euquinidine. The colour changes from yellow to rose, and finally to purplish-red.[83]

A sensitive and characteristic test for strychnine consists in treatment of the alkaloid salt solution with hydrochloric acid and zinc amalgam, and finally with potassium ferricyanide. In the presence of quantities down to 0·001 milligram of strychnine, a pink to rose-red coloration is obtained.[83] Various colour reactions of emetine have also been described.[84]

Pyrrole reacts with p-dimethylaminobenzaldehyde in an analogous manner to indole, and this must be borne in mind when applying Ehrlich's test.[85]

Quantitative.—A new form of absorption apparatus for elementary analysis has been devised, in which the carbon dioxide is absorbed by potassium hydroxide solution, and special precautions are used in drying the gas.[86] Certain organic substances, such as methyl esters and chloro-compounds, may be quantitatively oxidised by means of a mixture of sulphuric and chromic acids, the chlorine in the latter compounds being retained by an amalgamated copper spiral preceding the burette in which the carbon dioxide is measured.[87] Another new method of estimating carbon and hydrogen in organic compounds is based on their combustion in contact with platinum and cerium dioxide.[88]

Fusion with an alkaline mixture containing alkali nitrates, precipitation of the carbonate as calcium carbonate from a solution of the fused mass, and titration of the washed precipitate with hydrochloric acid, has been recommended for the estimation of carbon.[89]

A simple and rapid method of estimating halogens in organic compounds is to volatilise the substance with air through a quartz

[81] M. Guerbet, *Compt. rend.*, 1920, **171**, 40 ; *A.*, ii, 517.

[82] D. Ganassini, *Arch. ital. biol.*, 1919, **69**, 73 ; *A.*, ii, 339.

[83] H. E. Buc, *J. Assoc. Off. Agric. Chem.*, 1919, **3**, 193 ; *A.*, ii, 397.

[84] A. Lahille, *Arch. méd. exp.*, **27**, 336 ; *A.*, ii, 134.

[85] E. Salkowski, *Biochem. Zeitsch.*, 1920, **103**, 185 ; *A.*, ii, 566.

[86] F. Friedrichs, *Zeitsch. angew. Chem.*, 1919, **32**, 388 ; *A.*, ii, 192.

[87] J. Guyot and L. J. Simon, *Compt. rend.*, 1920, **170**, 734 ; *A.*, ii, 332.

[88] K. Sumikura, *J. Tokyo Chem. Soc.*, 1919, **40**, 593 ; *A.*, ii, 126.

[89] L. Lescœur, *J. Pharm. Chim.*, 1920, [vii], **21**, 257 ; *A.*, ii, 332.

tube heated at 900—1000°, to absorb the products of combustion in sodium hydroxide solution containing sodium sulphite, and, after oxidising the excess of the latter with potassium permanganate, to estimate the halogen by Volhard's process.[90]

In using Kjeldahl's process for the estimation of nitrogen in aromatic nitro-compounds, it should be noted that accurate results may be obtained with ortho-compounds, but that those given by meta- and para-derivatives will be much too low.[91]

Estimation of nitro-groups by reduction with stannous chloride and titration of the excess of the reagent with iodine gives too low results with mononitrotoluenes, owing to the formation of p-chlorotoluidines, whilst the use of titanous chloride gives results about 3 per cent. too low in the case of o-nitrotoluene.[92] The low results given by a-nitronaphthalene and similar compounds may be obviated by substituting titanous sulphate for titanous chloride, and thus preventing chlorination.[93] Diazo-compounds, such as benzenediazonium chloride, may be titrated in hydrochloric acid solution by means of titanous chloride, with suitable indicators.[94]

A method for the estimation of methyl alcohol has been based on its oxidation with sulphuric acid and potassium dichromate, and gravimetric estimation of the carbon dioxide produced or volumetric estimation of the excess of dichromate.[95] In another method, the methyl alcohol is oxidised by means of ammonium persulphate, and the resulting formaldehyde estimated colorimetrically.[96]

For the estimation of ethylene glycol, oxidation with potassium dichromate and sulphuric acid, as in glycerol analysis, gives trustworthy results, but the acetin method is not applicable to dilute solutions of the glycol.[97]

An apparatus for estimating the carbon dioxide formed in the fermentation of sugars has been devised, and the method has been shown to be applicable to the differentiation of yeasts and enzymes by fermentation with appropriate sugars.[98]

[90] W. A. van Winkle and G. McP. Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 333; *A.*, ii, 328.

[91] B. M. Margosches and E. Vogel, *Ber.*, 1919, **52**, [B], 1992; *A.*, ii, 50.

[92] D. Florentin and H. Vandenberghe, *Bull. Soc. chim.*, 1920, [iv], **27**, 158; *A.*, ii, 271.

[93] T. Callan, J. A. R. Henderson, and N. Strafford, *J. Soc. Chem. Ind.*, 1920, **39**, 86T; *A.*, ii, 331.

[94] E. Knecht and L. Thompson, *J. Soc. Dyers and Col.*, 1920, **36**, 215; *A.*, ii, 647.

[95] A. Heiduschka and L. Wolff, *Pharm. Zentr.-h.*, 1920, **61**, 361; *A.*, ii, 515.

[96] S. B. Schryver and C. C. Wood, *Analyst*, 1920, **45**, 164; *A.*, ii, 393.

[97] B. Müller, *Chem. Zeit.*, 1920, **44**, 513; *A.*, ii, 515.

[98] A. Slator, *J. Soc. Chem. Ind.*, 1920, **39**, 149T; *A.*, ii, 448.

, Sucrose may be accurately estimated by a cryoscopic method.[99] For the estimation of sugars by inversion, chemical catalysts, such as benzenesulphonic acid, have advantages over enzymes.[1] The optical rotation of lævulose is destroyed by heating the sugar for seven hours with dilute hydrochloric acid, whereas that of dextrose is not affected. This has been made the basis of a method of estimating these sugars.[2] In the case of fruit juices, however, the most trustworthy method is to calculate the proportions of the respective sugars from the cupric-reducing power and the iodine value, the latter being characteristic for each sugar.[3] Another method of estimating dextrose has been based on the action of potassium cyanide for two days at 20°, and estimation of the excess of the reagent, or measurement in the change in rotation of the dextrose.[4]

A modification of the phenylhydrazine method for estimating pentosans consists in distilling the substance with sulphuric acid and estimating the furfuraldehyde by precipitation as hydrazone, and determination of the excess of phenylhydrazine in the filtrate.[5]

The coloration given by phenol when heated with Millon's reagent and nitric acid affords a means for its colorimetric estimation in the presence of other phenols.[6] Another method of estimating phenol is based on its titration with a solution of a diazonium compound, hydroxyazo-compounds being formed in the reaction.[7]

The conditions under which phenolphthalein combines quantitatively with iodine to form tetraiodophenolphthalein have been investigated, and a gravimetric method based on them.[8]

Silico- and phospho-tungstic acids are suitable reagents for the gravimetric and volumetric estimation of alkaloids under specified conditions, phosphotungstic acid being preferable in the case of aconitine and nicotine.[9] For the quantitative separation of strychnine from quinine, advantage has been taken of the fact that the former is only very slightly soluble in ethyl ether, and is left

[99] H. H. Dixon and T. G. Mason, *Sci. Proc. Roy. Dubl. Soc.*, 1920, **16**, 1 ; *A.*, ii, 395.

[1] E. Hildt, *Ann. Chim. anal.*, 1920, [ii], **2**, 103 : *A.*, ii, 395.

[2] F. Lucius, *Zeitsch. Nahr. Genussm.*, 1919, **38**, 177 ; *A.*, ii, 132.

[3] (Miss) H. M. Judd, *Biochem. J.*, 1920, **14**, 255 ; *A.*, ii, 395.

[4] J. Bougault and J. Perrier, *Compt. rend.*, 1920, **170**, 1395 ; *A.*, ii, 452.

[5] P. Menaul and C. T. Dowell, *J. Ind. Eng. Chem.*, 1919, **11**, 1024 ; *A.*, ii, 200.

[6] R. M. Chapin, *ibid.*, 1920, **12**, 771 ; *A.*, ii, 645.

[7] R. M. Chapin, *ibid.*, 568 ; *A.*, ii, 563.

[8] S. Palkin, *ibid.*, 1920, **12**, 766 ; *A.*, ii, 643.

[9] A. Heiduschka and L. Wolff, *Schweiz-Apoth. Zeit.*, 1920, **58**, 213, 229 ; *A.*, ii, 780.

in the aqueous solution on extraction with ether in the presence of ammonia.[10] Reference may also be made to a method of estimating codeine by treatment of the plant extract with calcium hydroxide, and extraction of the filtrate with toluene.[11]

Tyrosine cannot be estimated quantitatively in the products of the hydrolytes of proteins by the method of Folin and Denis,[12] since the blue coloration is also given by tryptophan and other compounds in the mixture.[13]

It has been shown that the growth of yeast cells under specified conditions depends on the amount of so-called vitamins present, and a gravimetric method of estimating vitamins has been based on this fact.[14] The method has been found applicable to the estimation of the vitamin in food.[15] On the other hand, the results of other experiments have indicated that the test is influenced by so many factors as to have little, if any, value.[16]

Inorganic Analysis.

Qualitative.—Sodium alizarinsulphonate has been proposed as a sensitive indicator for the titration of mineral acids, and has the further advantage that it can be used both with ammonia and phosphoric acid.[17]

Several new schemes for the separation of cations into groups have been published. These include a modification of Petersen's method [18] of separating the cations of the third and fourth groups,[19] and a new method for the separation of various metals in the presence of phosphoric acid.[20] The use of thioacetic acid has been shown to offer several advantages over hydrogen sulphide as a reagent for the precipitation of the cations of Group II.[21]

Sensitive tests for manganic, ceric, cobaltic, and thallic compounds have been based on the fact that they give intense blue colorations with benzidine and other diphenyl derivatives.[22]

[10] A. R. Bliss, *J. Amer. Pharm. Assoc.*, 1919, **8**, 804 ; *A.*, ii, 276.
[11] H. E. Annett and H. Sen, *Analyst*, 1920, **45**, 321 ; *A.*, ii, 644.
[12] *J. Biol. Chem.*, 1912, **12**, 245 ; *A.*, 1912, ii, 1012.
[13] R. A. Gortner and G. E. Holm, *J. Amer. Chem. Soc.*, 1920, **42**, 1678 ; *A.*, ii, 643.
[14] R. J. Williams, *J. Biol. Chem.*, 1920, **42**, 259 ; *A.*, ii, 648.
[15] W. H. Eddy and H. C. Stevenson, *ibid.*, 1920, **43**, 295 ; *A.*, ii, 716.
[16] G. de P. Souza and E. V. McCollum, *ibid.*, 1920, **44**, 113 ; *A.*, i, 919.
[17] W. Mestrezat, *J. Pharm. Chim.*, 1920, [vii], **21**, 185 ; *A.*, ii, 263.
[18] *Zeitsch. anorg. Chem.*, 1910, **67**, 253 ; *A.*, 1910, ii, 654.
[19] P. de Pauw, *Chem. Weekblad*, 1920, **17**, 191 ; *A.*, ii, 451.
[20] H. Remy, *Zeitsch. anal. Chem.*, 1919, **58**, 385 ; *A.*, ii, 186.
[21] N. Alvarez, *Bol. minero soc. nac. min. Chile*, 1919, **31**, 181 ; *A.*, ii, 381.
[22] F. Feigl, *Chem. Zeit.*, 1920, **44**, 689 ; *A.*, ii, 710.

Turning to the specific tests for individual substances, it has been shown that iodic acid may be used as a distinctive microscopical reagent for the detection of ammonia, characteristic crystals of ammonium iodate being formed.[23]

The differences between the deposits formed by hydrogen arsenide, cacodylic acid, methylarsinic acid, and neosalvarsan in Marsh's test have been studied, and it has been found that the addition of platinum chloride to promote the evolution of hydrogen may fix some of the arsenic in the flask.[24] The best method of detecting arsenic in sulphur is by oxidation with bromine and nitric acid, and application of Gutzeit's test to the product.[25] A test for salts of tin has been based on the insolubility of stannous or stannic iodide in sulphuric acid. The yellow precipitate may be distinguished from the similar compound formed by arsenic by the fact that it is soluble in dilute hydrochloric acid. The corresponding antimony salt is brick-red and flocculent.[26] A distinctive test for osmium tetroxide is afforded by the blue coloration which it gives with pyrogallol, whilst the vapour may be identified by giving a permanent stain, due to the reduced osmium, with a slightly greasy finger-print.[27]

Xanthic acid may be used as a distinctive reagent for molybdenum,[28] but it is essential that oxalates should not be present, whilst copper, cobalt, nickel, iron, and uranium interfere with the test.[29]

For the detection of traces of cobalt, the coloration given by β-nitroso-α-naphthol is much more sensitive than that obtained with α-nitroso-β-naphthol.[30] Cobalt may be detected in the presence of nickel by means of potassium xanthate. The xanthates of both metals are precipitates, but the cobalt compound is insoluble in ammonia, whereas the nickel compound dissolves, forming a blue solution.[31]

Most cerous and ceric compounds give a bright blue coloration when moistened with a solution of benzidine in acetic acid, and the reaction may be used for detecting cerium in the presence of other metals of the ammonium sulphide group of rare earths, with the exception of thallium.[32]

[23] G. Denigès, *Compt. rend.*, 1920, **171,** 177 ; *A.,* ii, 555.

[24] D. Ganassini, *Boll. Chim. farm.*, 1919, **58,** 385 ; *A.,* ii, 51.

[25] H. S. Davis and M. D. Davis, *J. Ind. Eng. Chem.*, 1920, **12,** 479 ; *A.,* ii, 448.   [26] A. Mazuir, *Ann. Chim. anal.*, 1919, [ii], **2,** 9 ; *A.,* ii, 197.

[27] C. A. Mitchell, *Analyst*, 1920, **45,** 125 ; *A.,* ii, 335.

[28] S. L. Malowan, *Zeitsch. anorg. Chem.*, 1919, **108,** 73 ; *A.,* ii, 59.

[29] J. Koppel, *Chem. Zeit.*, 1919, **43,** 777 ; *A.,* ii, 58.

[30] I. Bellucci, *Gazzetta*, 1919, **49,** ii, 294 ; *A.,* ii, 194.

[31] L. Compin, *Ann. Chim. anal.*, 1920, [ii], **2,** 218 ; *A.,* ii, 559.

[32] F. Feigl, *Oesterr. Chem. Zeit.*, [ii], **22,** 124 ; *A.,* ii, 54.

Iodic acid has been found to be a useful microchemical reagent for calcium, strontium, or barium, the distinctive forms of the crystalline iodates being observed.[33] It may also be used to distinguish between the salts of barium and radium.[34]

For the detection of magnesium, advantage has been taken of the fact that it gives a bluish-violet coloration with an alcoholic solution of alkannin, the similar colorations given by strontium and manganese being distinguished by their behaviour after acidification.[35]

The applicability and sensitiveness of various reactions for potassium have been determined, and the most sensitive reagent has been found to be sodium–bismuth thiosulphate, which is capable of detecting 1 part in 57,000.[36]

The colour changes which take place in the diphenylamine reaction for nitrates have been studied, and a sensitive modification of the reagent devised for microchemical tests.[37] A blue coloration may be produced in the diphenylamine reagent by the presence of ferric salts in the sulphuric acid.   To prevent this, such acid should be boiled, and cooled to reduce the ferric salts.[38]

A sensitive test for nitrites in the presence of nitrates is the production of a red coloration on treating the solution successively with acetic acid, potassium oxalate solution, manganous sulphate, and hydrogen peroxide.[39] For the detection of phosphates in the presence of barium, a modification of Deniges' strychnine-molybdate reagent is sensitive, but must be freshly prepared.[40]

Quantitative.—It is in this branch of the subject that the greatest activity has been shown, and the contributions to different journals have been so numerous that it has been necessary to select only the more important for mention in this Report.

A method of using potassium chlorate as an original standard for the titration of alkali has been described. The chlorate is reduced by means of sulphur dioxide, the excess of the latter removed, and the sulphuric acid formed in the reduction titrated with alkali—$KClO_3 + 3SO_2 + 3H_2O = 3H_2SO_4 + KCl$.[41] Another suitable standard is potassium hydrogen phthalate, which contains

[33] G. Denigès, *Compt. rend.*, 1920, **170**, 996 ; *A.*, ii, 388.

[34] G. Denigès, *ibid.*, 1920, **171**, 633 ; *A.*, ii, 706.

[35] F. Eisenlohr, *Ber.*, 1920, **53**, [B], 1476 ; *A.*, ii, 708.

[36] O. Lutz, *Zeitsch. anal. Chem.*, 1920, **59**, 145 ; *A.*, ii, 509.

[37] E. M. Harvey, *J. Amer. Chem. Soc.*, 1920, **42**, 1245 ; *A.*, ii, 504.

[38] F. Haun, *Zeitsch. Nahr. Genussm.*, 1920, **39**, 355 ; *A.*, ii, 555.

[39] P. H. Hermans, *Pharm. Weekblad*, 1920, **57**, 462 ; *A.*, ii, 448.

[40] L. Débourdeaux, *Bull. Sci. pharmacol.*, 1920, **27**, 70 ; *A.*, ii, 505.

[41] H. B. van Valkenburgh, *J. Amer. Chem. Soc.*, 1920, **42**, 757 ; *A.*, ii, 387.

no water of crystallisation and is not hygroscopic.[42] In preparing the salt, it is advisable to crystallise it above 20°, to prevent the formation of a more acid salt.[43] A useful indicator for coloured liquids has been found in ferrous sulphide, the formation of which is prevented by a slight trace of acid. A crystal of pure ferrous ammonium sulphate is added to the solution, which is then treated with hydrogen sulphide, and titrated with alkali until a permanent black coloration is obtained.[44]

Various experiments have been made with salts of magnesium, zinc, mercury, and aluminium to determine the degree of accuracy obtainable in the acidimetric titration of the salts of heavy metals which form insoluble hydroxides.[45]

In the volumetric estimation of sulphates by oxidation of benzidine sulphate with potassium permanganate,[46] it is essential that the solution from which the benzidine sulphate is precipitated should be free from organic matter, iron, heavy metals, nitrates, and phosphates.[47]

A new volumetric reduction method with arsenic trioxide has been devised, in which an oxidising agent, such as a chlorate or chromate, is treated with excess of arsenic trioxide in the presence of hydrochloric acid, and the solution subsequently titrated with potassium bromate solution.[48]

Several new iodometric methods have been published. The conditions for the iodometric estimation of acids, more especially weak acids, have been investigated, and the applicability of various methods has been determined.[49] The direct estimation of chloric acid in a strongly acid medium gives too high results, owing to oxidation of hydrogen iodide, but Rupp's method[50] is trustworthy.[51] For the iodometric estimation of arsenic acid, the reacting mixture should be heated to 100° and contain specified proportions of potassium iodide and hydrogen chloride.[52]

Stannous tin may be more accurately estimated by a volumetric method in an acid solution. Titration with standard iodine solu-

[42] W. S. Hendrixson, *J. Amer. Chem. Soc.*, 1920, **42**, 724 ; *A.*, ii, 382.

[43] F. D. Dodge, *ibid.*, 1655 ; *A.*, ii, 628.

[44] J. Houben, *Ber.*, 1919, [B], 1613 ; *A.*, ii, 53.

[45] I. M. Kolthoff, *Zeitsch. anorg. Chem.*, 1920, **112**, 172 ; *A.*, ii, 709.

[46] G. W. Raiziss and H. Dubin, *J. Biol. Chem.*, 1914, **18**, 297 ; *A.*, 1914, ii, 671.

[47] P. L. Hibberd, *Soil Sci.*, 1919, **8**, 61 ; *A.*, ii, 191.

[48] F. de Bacho, *Annali Chim. Appl.*, 1919, **12**, 153 ; *A.*, ii, 188.

[49] I. M. Kolthoff, *Pharm. Weekblad*, 1920, **57**, 53 ; *A.*, ii, 121.

[50] E. Rupp, *Zeitsch. anal. Chem.*, 1917, **56**, 580 ; *A.*, 1918, ii, 125.

[51] I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 460 ; *A.*, ii, 190.

[52] P. Fleury, *J. Pharm. Chim.*, 1920, [vii], **21**, 385 ; *A.*, ii, 448.

tion in the presence of hydrochloric acid is satisfactory in the case of many compounds.[53] The iodometric estimation of chromium gives too high results, owing to the influence of atmospheric oxygen on the reaction.[54]

To obtain accurate results in the iodometric estimation of potassium ferricyanide, the acid concentration must be kept sufficiently high and the time of the reaction restricted.[55]

A new volumetric method of estimating nickel has been based on the titration of the acid which is liberated in the reaction with dimethylglyoxime.[56]

Further work on the use of organic solvents for the quantitative separation of metals has shown that the method of progressive precipitation previously described[57] is suitable for the separation of magnesium from sodium and potassium, the salts of the latter metals being precipitated first by means of alcohol and ether.[58]

New applications of the use of cupferron (the ammonium salt of nitrosophenylhydroxylamine) have been published. The reagent gives good results in the estimation of iron, copper, titanium, zirconium, thorium, and vanadium in the absence of certain interfering substances, but in many cases offers no advantage over previous methods.[59] It is most serviceable for the separation of copper from arsenic, and especially from antimony. Like α-nitroso-β-naphthol, it is a useful reagent for separating elements into groups.[60] In neutral solution it gives precipitates with all metals except the alkali metals, and the precipitates may be separated into two groups by their behaviour towards chloroform and dilute acids.[61] If corrections for the solubility of the precipitate be applied, iron may be accurately separated from manganese by cupferron.[62] A trustworthy method has also been worked out for the use of the reagent in the separation of tin and antimony.[63]

A simple method of estimating mercury is to cause it to be

[53] J. G. F. Druce, *Chem. News*, 1920, **121**, 173 ; *A.*, ii, 710.

[54] O. Meindl, *Zeitsch. anal. Chem.*, 1919, **58**, 529 ; *A.*, ii, 390.

[55] I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 1618 ; *A.*, ii, 67.

[56] J. Holluta, *Monatsh.*, 1919, **40**, 281 ; *A.*, ii, 57.

[57] S. Palkin, *J. Amer. Chem. Soc.*, 1916, **38**, 2326 ; *A.*, 1917, ii, 43.

[58] *Ibid.*, 1920, **42**, 1618 ; *A.*, ii, 637.

[59] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, 1920, **12**, 344 ; *A.*, ii, 390.

[60] I. Bellucci and A. Chiucini, *Gazzetta*, 1919, **49**, ii, 187 ; *A.*, ii, 54.

[61] V. Auger, *Compt. rend.*, 1920, **170**, 995 ; *A.*, ii, 391.

[62] E. H. Archibald and R. V. Fulton, *Trans. Roy. Soc. Canada*, 1919, **13**, [iii], 243 ; *A.*, ii, 512.

[63] A. Kling and A. Lassieur, *Compt. rend.*, 1920, **170**, 1112 ; *A.*, ii, 452.

deposited on a coil of copper gauze, and to estimate the amount of the deposit by the loss in weight after heating the coil in a current of hydrogen.[64]

Arsenic may be separated from antimony, tin, copper, lead, mercury, and iron by a modification of the distillation method, whilst antimony may be separated from tin by volatilising antimony chloride at 155—165° from solutions to which phosphoric acid has been added to render the tin non-volatile.[65] A modification of the Marsh-Berzelius test has been described in which the hydrogen arsenide is conducted over red-hot copper, which retains the arsenic as arsenides. The results are about 1·4% too low, possibly owing to retention of arsenic in the flask in the form of a stable complex.[66]

In order to obtain a precipitate of secondary zirconium phosphate of constant composition in the precipitation of zirconium by the phosphate method, the solution should contain from 2 to 20 per cent. of sulphuric acid, and an excess of diammonium hydrogen phosphate ten to one hundred times in excess of the theoretical quantity should be added.[67] A new method, applicable to zirconia ores, is to precipitate the zirconium with selenious acid, and to ignite the basic selenite, which leaves a residue of zirconia.[68]

The difficulty of precipitating molybdenum quantitatively as sulphide may be obviated by having a sufficient quantity of formic acid in the solution, and seeing that the whole of the molybdenum is present as molybdate.[69]

From a study of various methods of estimating uranium, the conclusion has been drawn that precipitation with ammonium sulphide or with ammonia gives the most trustworthy results. In either case, the precipitate leaves uranoso-uranic oxide on ignition.[70] Precipitation of uranium as uranyl ammonium phosphate is also a good method, but has the drawback that the ignited uranyl pyrophosphate rapidly absorbs moisture.[71] For the estimation of minute quantities of uranium, a colorimetric method has been based on the red coloration given by uranyl salts with sodium salicylate.[72]

[64] H. B. Gordon, *Analyst*, 1920, **45**, 41 ; *A.*, ii, 194.

[65] W. Strecker and A. Riedemann, *Ber.*, 1919, **52**, [B], 1935 ; *A.*, ii, 51.

[66] B. S. Evans, *Analyst*, 1920, **45**, 8 ; *A.*, ii, 125.

[67] G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1919, **41**, 1801 ; *A.*, ii, 60.

[68] M. S. Smith and C. James, *ibid.*, 1920, **42**, 1764 ; *A.*, ii, 710.

[69] J. Stěrba-Böhm and J. Vostřebal, *Zeitsch. anorg. Chem.*, 1920, **110**, 81 ; *A.*, ii, 335.   [70] R. Schwarz, *Helv. Chim. Acta*, 1920, **3**, 330 ; *A.*, ii, 391.

[71] C. A. Pierre, *J. Ind. Eng. Chem.*, 1920, **12**, 60 ; *A.*, ii, 197.

[72] Müller, *Chem. Zeit.*, 1919, **43**, 739 ; *A.*, ii, 60.

The perchlorate method for the estimation of potassium gives accurate results under specified conditions.[73] The method previously described[74] is rendered more trustworthy by extracting the sodium perchlorate with alcohol containing perchloric acid, instead of with a saturated solution of potassium perchlorate.[75] By using aniline perchlorate in place of perchloric acid, the process is rendered more rapid than any other method of estimating potassium.[76] The proportion of potassium in the mixed precipitate of potassium and sodium cobaltinitrite may be calculated from a gravimetric or electrolytic estimation of the cobalt.[77] Another method of estimating the proportions of the two metals in mixtures of the salts is to convert them into nitrates and determine the melting points.[78]

Chromic acid liberates bromine quantitatively from bromides at the ordinary temperature, and the bromine may be removed by aspiration, whereas chlorides under the same conditions yield only traces of chlorine. A method of estimating bromine in mineral waters has been based on these facts.[79]

The conditions for effecting the quantitative estimation of phosphoric acid by precipitating and weighing it as ammonium phosphomolybdate have been investigated, and a trustworthy method devised. For the nephelometric estimation of traces of phosphoric acid, the use of a reagent prepared by the interaction of strychnine sulphate and sodium molybdate gives excellent results.[80]

Electrochemical Analysis.

There have been relatively few contributions to gravimetric electrolytic methods of analysis, but much work has been done in connexion with the investigation of methods of electrometric titration and their extension to further substances.

It has been shown that in many cases the end-point of a titration is sharply indicated by measurement of the terminal voltage between two electrodes, one of which is immersed in the solution

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[73] R. L. Morris, *Analyst*, 1920, **45**, 349 ; *A.*, ii, 707.

[74] G. P. Baxter and M. Kobayashi, *J. Amer. Chem. Soc.*, 1917, **39**, 249 ; *A.*, 1917, ii, 270.

[75] G. P. Baxter and M. Kobayashi, *ibid.*, 1920, **42**, 735 ; *A.*, ii, 388.

[76] S. B. Kuzirian, *Proc. Iowa. Acad. Sci.*, 1917, **24**, 547 ; *A.*, ii, 450.

[77] P. Wenger and C. Hémen, *Ann. Chim. anal.*, 1920, [ii], **2**, 198 ; *A.*, ii, 556.

[78] A. Quartaroli, *Gazzetta*, 1920, **50**, ii, 64 ; *A.*, ii, 635.

[79] W. F. Baughman and W. W. Skinner, *J. Ind. Eng. Chem.*, 1919, **11**, 954 ; *A.*, ii, 48.

[80] H. Kleinmann, *Biochem. Zeitsch.*, 1919, **99**, 150 ; *A.*, ii, 634.

under examination, and is capable of yielding the same ions to the solution, whilst the second, or comparison electrode, is composed of the same metal as the first and of the precipitate or other product of the reaction. Owing to the slow action of the electrode, the method does not give sharp results in the titration of hydrogen-ion concentration.[81] A hydrogen electrode giving a sharp end-point in acidimetric titrations has been described, and shown to be suitable for the estimation of strong acids in the presence of weak acids.[82] Other electrometric methods may be used for the estimation of weak acids, such as acetic acid, in the presence of strong acids, such as hydrochloric acid.[83] A simple method of acidimetric or alkalimetric titration is to connect the solution to be titrated with another of known P_H value, each being provided with a hydrogen electrode, and to continue the titration until the same hydrogen-ion concentration is shown by both solutions.[84] Carbonic acid and its salts in dilute solution can be titrated in this way,[85] whilst phosphoric acid in dilute solution behaves like a mono- or di-basic acid, the first end-point being sharp, whilst the second is less distinct.[86]

A method for the electrometric estimation of arsenic in coloured solution is to titrate arsenic trioxide with iodine solution in the presence of sodium hydrogen carbonate, and to titrate arsenic pentoxide in sulphuric acid solution at 95° with sodium iodide solution.[87] Lead and zinc salts may be accurately titrated with potassium ferrocyanide, but in the case of other metals the precipitates are not constant in composition.[88]

The fact that mercuric acetate forms a stable, complex compound with allyl alcohol has been utilised for the electrometric titration of that alcohol by means of a standard solution of the mercury salt.[89]

The presence of soluble ferricyanides or chlorides in moderate proportion does not interfere with the titration of ferrocyanides with potassium permanganate solution, but salts yielding pre-

[81] W. D. Treadwell and L. Weiss, *Helv. Chim. Acta*, 1919, **2**, 680; *A.*, ii, 119.

[82] W. D. Treadwell and L. Weiss, *ibid.*, 1920, **3**, 433; *A.*, ii, 553.

[83] I. M. Kolthoff, *Rec. trav. chim.*, 1920, **39**, 280; *A.*, ii, 327.

[84] P. E. Klopsteg, *Science*, 1920, **52**, 18; *A.*, ii, 700.

[85] I. M. Kolthoff, *Zeitsch. anorg. Chem.*, 1920, **112**, 155; *A.*, ii, 705.

[86] I. M. Kolthoff, *ibid.*, 165; *A.*, ii, 705.

[87] C. S. Robinson and O. B. Winter, *J. Ind. Eng. Chem.*, 1920, **12**, 775; *A.*, ii, 635.

[88] Erich Müller, *Zeitsch. angew. Chem.*, 1919, **32**, 351; *A.*, ii, 54.

[89] E. Biilmann, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1919, **5**, 1; *A.*, i, 131.

cipitates with either ferro- or ferri-cyanides must not be present.[90]

The alcoholic strength of beer or wine may be rapidly estimated by distillation with magnesium oxide (after removal of carbon dioxide), treatment of the distillate with oxalic acid solution, and determination of the specific conductivity of the mixture and of the original oxalic acid solution. The required result is then obtained by the use of a formula.[91]

Amino-acids may be estimated alkalimetrically by means of the hydrogen electrode, and a simple method for the purpose has been devised.[92] The conductometric process has also been adapted to the titration of phenols, cresols, and certain hydroxy-acids.[93] A similar process has been worked out for the estimation of alkaloids and their salts, the alkaloids themselves being titrated with acid, whilst alkaloid salts are titrated with alkali.[94]

An indirect method for the electrolytic estimation of halogens has been based on the fact that the solution can be electrolysed by means of a silver anode, with the formation of an adherent deposit on the anode, and without precipitation in the solution, provided that an anode potential of 0·59 volt is not exceeded.[95]

When an ammoniacal solution of nickel and a salt of arsenic acid is electrolysed, the nickel is quantitatively precipitated without any arsenic, whereas cobalt under the same conditions carries down a certain proportion of arsenic.[96]

Reference may also be made to methods in which rotating reductors are used in the estimation of iron[97] and of molybdenum.[98]

Water Analysis.

The principal contributions to the analysis of drinking-water have been in connexion with the dissolved carbon dioxide. It has been shown that the simple mass-law equation of the primary ionisation of carbonic acid enables the hydrogen-ion concentration of natural waters to be approximately calculated.[99]

In titrating the free carbon dioxide and that present as hydrogen

[90] G. L. Kelley and R. T. Bohn, *J. Amer. Chem. Soc.*, 1919, **41**, 1776 ; *A.*, ii, 134.

[91] I. M. Kolthoff, *Rec. trav. chim.*, 1920, **39**, 126 ; *A.*, ii, 198.

[92] E. L. Taube, *J. Amer. Chem. Soc.*, 1920, **42**, 174 ; *A.*, ii, 396.

[93] I. M. Kolthoff, *Zeitsch. anorg. Chem.*, 1920, **112**, 187 ; *A.*, ii, 711.

[94] I. M. Kolthoff, *ibid.*, 196 ; *A.*, ii, 781.

[95] J. H. Reedy, *J. Amer. Chem. Soc.*, 1919, **41**, 1898 ; *A.*, ii, 122.

[96] N. H. Furman, *ibid.*, 1920, **42**, 1789 ; *A.*, ii, 710.

[97] W. Scott, *J. Ind. Eng. Chem.*, 1919, **11**, 1135 ; *A.*, ii, 128.

[98] W. Scott, *ibid.*, 1920, **12**, 578 ; *A.*, ii, 578.

[99] R. E. Greenfield and G. C. Baker, *ibid.*, 1920, **12**, 989 ; *A.*, ii, 771.

carbonate in moorland waters, errors are caused by the presence of weak organic acids which are simultaneously titrated. To determine the solvent action of such waters on limestone, the water is shaken at intervals with powdered marble in a closed flask, and a portion then titrated with $N/10$-acid. The difference between the result and that obtained without the addition of marble gives the amount of calcium carbonate dissolved.[1]

It has been shown by Tillmanns and Heublein[2] that the free carbon dioxide in soft water has a much greater solvent action on calcium carbonate than the same amount of carbon dioxide in hard water. In the case of waters containing iron hydrogen carbonate, the semi-combined and the combined carbon dioxide in the iron compound are titrated simultaneously with the free carbon dioxide, and, as a correction, 1·1 milligram of carbon dioxide must be deducted for each milligram of ferric oxide present.[3]

In using Escaïch's colour test for nitrites[4] in water, the results are uncertain in the presence of chlorides, which must therefore be removed by means of silver nitrate before applying the test.[5]

<div align="right">C. AINSWORTH MITCHELL.</div>

[1] V. Rodt, *Chem. Zeit.*, 1920, **44**, 469 ; *A.*, ii, 507.

[2] *Gesundheits-Ing.*, 1912, **35**, 669 ; *A.*, 1913, ii, 51.

[3] H. Noll, *Zeitsch. angew. Chem.*, 1920, **33**, i, 182 ; *A.*, ii, 555.

[4] *J. Pharm. Chim.*, 1918, [vii], **17**, 395 ; *A.*, 1918, ii, 273.

[5] A. Escaïch, *ibid.*, 1920, [vii], **22**, 138 ; *A.*, ii, 644.

PHYSIOLOGICAL CHEMISTRY.

SINCE writing last year's Report the deaths of the following have occurred: G. von Bunge, Sir Thomas Fraser, Armand Gautier, Wilhelm Pfeffer, Max Siegfried, and Nathan Zuntz. Von Bunge was Professor of Physiological Chemistry at Basle, and the author of a well-known text-book. His best known research was concerned with the mineral constituents of blood and milk. Fraser was for many years professor of materia medica at Edinburgh; he introduced Calabar beans into medicine in the early sixties, but it is chiefly during the last decade that physostigmine has attracted much attention from organic chemists. A study of arrow poisons led him to the therapeutic application of strophanthin; he made also an extensive study of snake venoms, and his name is associated with that of Crum Brown in the generalisation that quaternary salts of organic bases have a curare-like action. Gautier, the veteran of French biochemistry, originally received a medical training, but became later assistant to Wurtz and was for many years Professor of Medical Chemistry at Paris. He is known for his studies on ptomaines and on the occurrence of the biologically rare elements (fluorine, arsenic, etc.). He also worked on arsenical drugs and questions of hygiene, food and general chemistry.

Pfeffer's "Osmotische Untersuchungen," published in 1877, became known five years later to Van't Hoff, through the latter's botanical colleague, de Vries, and thus became one of the most fruitful stimuli ever given by biology to physical science. Doubtless Pfeffer owed some of his success to his early training as a chemist; his doctor's dissertation related to an organic chemical problem. Siegfried also began as an organic chemist; as assistant to Drechsel he was diverted to physiological chemistry. He became extraordinary and (1919) ordinary professor of this subject at Leipzig. His best known work is on the extractives of muscle and the kyrines. Zuntz, on the other hand, was by training a physiologist, and an early appointment at the Agricultural College of Poppelsdorf, near Bonn, determined his career. He was mainly

concerned with nutrition and gaseous interchange, for which he worked out exact methods of gas analysis. At Berlin he would rejoice in later years in showing visitors his respiration chamber capable of accommodating an ox.

In July, 1920, an international congress of Physiology met at Paris; the next meeting is to take place at Edinburgh in 1922. In France the Société de Chimie Biologique, founded in 1914, has resumed the publication of its *Bulletin*. After two pre-war numbers, the third followed in October, 1919, and others during the present year. Besides original papers there have been occasional résumés of current questions, valuable on account of their lucidity. During the year a new periodical of biochemical interest has begun under the title of the *British Journal of Experimental Pathology*.

In America a series of monographs has now also been started, "on experimental biology and general physiology." Some of those announced are on more or less chemical subjects. In the series of "Monographien aus dem Gesamtgebiet der Physiologie der Pflanzen und der Tiere," there appeared last year "Die Narkose in ihrer Bedeutung für die allgemeine Physiologie," by H. Winterstein, and this year, "Die biogenen Amine," by M. Guggenheim. The latter is an excellent up-to-date account of the chemical and physiological properties of the simpler bases of biological interest, written by a well-known worker on the subject. The production of large hand-books has been resumed in Germany to some extent. A new "Handbuch der biologischen Arbeitsmethoden" is appearing under the general editorship of E. Abderhalden. It will replace the "Biochemische Arbeitsmethoden," now out of print, and is on a very extensive scale; there will be 13 parts, of which the first, dealing with purely chemical methods, is of primary interest to us here. By the publication, towards the end of 1920, of the second half of his "Lehrbuch der physiologischen Chemie." E. Abderhalden has completed the fourth edition. The first half appeared more than a year ago. The second half (which actually bears the date 1921) has been almost entirely rewritten. It is a few pages shorter than Vol. II. of the 1915 edition, in spite of a new chapter on vitamins. In 1920 there has also appeared Part II. of the first volume of a "Handbuch der experimentellen Pharmakologie," edited by A. Heffter. This, the first instalment of the whole work, deals with many important alkaloids, for example, cinchona alkaloids and derivatives, colchicine, cocaine, ipecacuanha alkaloids, strychnine. The manuscript was prepared before the war and although some articles have apparently been revised to 1918, others do not extend beyond 1913, and do not take into

account the therapeutic discoveries of the war. The book will, however, doubtless interest some chemists. Two outstanding French books on bacteriology should also be mentioned here, both the result of scientific isolation during the war: "Traité de l'immunité dans les maladies infectueuses," by J. Bordet, and "L'infection bacillaire et la tuberculose chez l'homme et chez les animaux," by A. Calmette. The former book especially should appeal to anyone seeking a chemical basis for immunological phenomena.

Metabolism of Carbohydrates.

The hypothesis of Chauveau, that fats only become a source of muscular energy after they have been transformed into carbohydrates, was shown to be untenable some twenty years ago by the work of Zuntz and his pupils, who drew the conclusion that fats and carbohydrates are isodynamic, that is, that in both these classes of foodstuffs the same fraction of the heat of combustion can be converted into work. The researches of Fletcher, Hopkins, A. V. Hill and others have, however, made it pretty certain that the process of muscular contraction is associated with chemical reactions of substances closely related to the carbohydrates, and then it becomes difficult to understand that the utilisation of fats is not attended by some loss of energy. These considerations have led A. Krogh and K. G. Lindhard [1] to an important reinvestigation of "the relative value of fat and carbohydrate as sources of muscular energy." Their method involved the determination of the respiratory quotient of a subject working an ergometer in a respiration chamber, and they determined this quotient within 0·005 by very accurate analysis of the air passing through the chamber. In connexion with this A. Krogh has published subsidiary papers [2] on a gas analysis apparatus accurate to 0·001 per cent., and on the calibration, accuracy and use of gas meters, which papers may be of use to non-biological chemists. Krogh and Lindhard find that the net expenditure of energy (after deducting the standard meta- bolism) necessary to perform the equivalent of one calorie of technical work on the ergometer varied from 4–5·5 calories. In the three best series of experiments it was 4·6 cal. when fat alone was catabolised (R.Q. = 0·71) and 4·1 cal. for carbohydrate alone (R.Q. = 1·0). This shows a waste of energy from fat of 0·5 cal., or 11 per cent. of its heat of combustion. The authors suggest as a working hypothesis that both during rest and work the proportion of fat to carbohydrate katabolised is a function of the available

[1] *Biochem. J.*, 1920, **14**, 290 ; *A.,* i, 692.
[2] *Ibid.*, 267, 282 ; *A.,* ii, 553, 630.

supply of these substances. With the respiratory quotient below 0·8 carbohydrate is formed from fat and provisionally stored; the reverse transformation takes place with a respiratory quotient above 0·9.

A novel aspect of the metabolism of reducing sugars is dealt with by J. A. Hewitt and J. Pryde,[3] who find that solutions of d glucose introduced into the intestine of the living animal undergo rapid downward mutarotation from +52·5° to below +19°, and in one experiment the solution even became lævorotatory. On withdrawal from the intestine the reverse change takes place more slowly, until the original rotation of α- and β-glucoses in equilibrium is reached. This change is not due to preferential absorption of the α-form or to disaccharide formation, but probably to the formation of γ-glucose in excess of any amount normally present in glucose solution which has reached an equilibrium.

Proteins.

Various classifications of proteins have been discussed by P. Thomas.[4] The two principal methods for determining the degree of hydrolysis of a protein are that of Van Slyke, who determines the free amino-groups, and that of Sörensen, who titrates the carboxyl groups. The former method has been elaborated into an indirect analysis of amino-acids in groups, of which the largest is that with amino-nitrogen, comprising glycine, alanine, serine, phenylalanine, tyrosine, valine, the three leucines, aspartic and glutamic acids. This large group A. C. Andersen[5] subdivides further by neutralising the solution with sodium hydroxide in the way indicated by Sörensen for his formol titration. Under these conditions only aspartic and glutamic acids combine with one equivalent of sodium hydroxide, and the monocarboxylic acids remain in the free state. On ashing such a solution the amount of sodium carbonate in the residue is equivalent to the monamino-dicarboxylic acids present.

Amino-Acids.

H. D. Dakin[6] has synthesised racemic β-hydroxyglutamic acid, of which an active modification was discovered by him in casein.[7] The synthesis presented unexpected difficulties and several attempted methods failed or gave only minute yields. The best

[3] *Biochem. J.*, 1920, **14**, 395 ; *A.*, i, 508.
[4] *Bull. Soc. Chim. biol.*, 1920, **2**, 112 ; *A.*, i, 644.
[5] *Kong. Vet. og Landbohöjskole Aarskrift*, 1917, 308 ; *A.*, ii, 647.
[6] *Biochem. J.*, 1919, **13**, 398 ; *A.*, i, 294.
[7] *Ann. Reports*, 1919, **16**, 153 ; *A.*, 1919, i, 150.

results were obtained by the following method. Glutamic acid was converted by potassium cyanate into α-carbamidoglutaric and then into hydantoinpropionic acid (I). The action of bromine on

$$
\begin{array}{cccc}
\begin{array}{l}
\text{CO--NH} \\
\text{CH·NH}
\end{array}\!\!>\!\!\text{CO} &
\begin{array}{l}
\text{CO--NH} \\
\text{CH·NH}
\end{array}\!\!>\!\!\text{CO} &
\begin{array}{l}
\text{CO--NH} \\
\text{CH·NH}
\end{array}\!\!>\!\!\text{CO} &
\begin{array}{l}
\text{CO}_2\text{H} \\
\text{CH·NH}_2
\end{array} \\
\text{CH}_2 & \text{CHBr} & \text{CH} & \text{CH·OH} \\
\text{CH}_2 & \text{CH}_2 & \text{CH} & \text{CH}_2 \\
\text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{(I.)} & \text{(II.)} & \text{(III.)} & \text{(IV.)}
\end{array}
$$
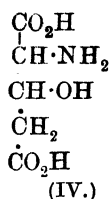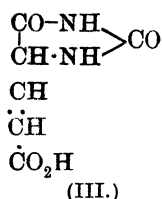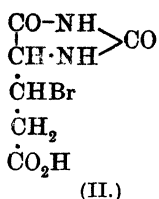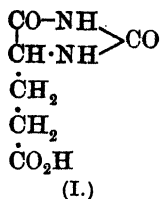
the latter is complex; after bromine enters the molecule it is split off again as hydrogen bromide, introducing a double bond in the βγ-position, but when the bromination is carried out in glacial acetic acid saturated with hydrogen bromide, the latter is added on again and *i*-hydantoin-β-bromopropionic acid (II) results. On boiling this with water hydantoinacrylic acid (III) is formed with the double bond in the required αβ-position. This acid is boiled with baryta solution until half the nitrogen has been evolved as ammonia, indicating the complete opening of the hydantoin ring. At the same time a molecule of water is added and inactive β-hydroxyglutamic acid (IV) results, in a yield of 20 per cent. of the hydantoinacrylic acid or 2 per cent. of the glutamic acid employed. The original paper should be consulted by organic chemists desirous of effecting a smoother synthesis. A secondary result of Dakin's experiments was the preparation of malic semi-aldehyde $CHO·CH(OH)·CH_2·CO_2H$, which, however, does not lend itself to the application of the Strecker synthesis.

Apart from casein Dakin has now also found his new amino-acid in glutenin (2·4 per cent.) and in gliadin (1·8 per cent.); D. B. Jones and C. O. Johns[8] have also isolated it from stizolobin, the globulin of the Chinese velvet bean (yield 2·8 per cent.). In dogs rendered diabetic by phloridzin, β-hydroxyglutamic acid appears as "extra glucose," as is the case with glutamic acid, proline and ornithine, and the amount was found to correspond closely with that derivable from three of the five carbon atoms. Dakin considers that β-hydroxyglutamic acid very likely arises in the body from glutamic acid and would then constitute an example of "β-oxidation" such as is known to occur in fatty acids, but has not yet been observed in amino-acids. Thus proline would be converted to glutamic acid via pyrrolidonecarboxylic acid, and ornithine would also be converted into glutamic acid. The latter would then be changed into dextrose by successive conversion into

8 *J. Biol. Chem.*, 1919, **40**, 435 ; *A.*, i, 191.

β-hydroxyglutamic, malic and lactic acids, two molecules of the latter forming the hexose. In support of this view Dakin has oxidised β-hydroxyglutamic to malic acid *in vitro* and the biochemical conversion of the latter into sugars has been brought about in several ways.

A new method for preparing esters of amino-acids has been published by F. W. Foreman.[9] It consists in converting the amino-acids into their dry lead salts, which are suspended in absolute alcohol and esterified by saturating with hydrogen chloride. After removal of the free hydrochloric acid and the alcohol, the ester hydrochlorides are dissolved in dry chloroform and the free esters liberated by shaking with anhydrous barium hydroxide. Thus the considerable loss of esters by hydrolysis is avoided, which occurs in aqueous solution. The process has been applied to caseinogen and some of the deficit has been accounted for, without however taking Dakin's above-mentioned hydroxyglutamic acid into account. Although amino-acids are usually formulated with tervalent nitrogen and free carboxyl, they might also be represented as internal anhydrides of an acid with an ammonium hydroxide. This "betaine" formula, originally suggested by R. Willstätter, was supported experimentally by A. Geake and M. Nierenstein,[10] who found that amino-acids are not methylated in ethereal suspension by diazomethane. J. Herzig and K. Landsteiner[11] have confirmed this observation as regards glycine and alanine, but find that in other amino-acids the carboxyl group is slowly and at least partly esterified, so that in them there appears to be an equilibrium between the two forms thus:—

$$\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \quad \text{and} \quad \overline{\text{NH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}}.$$
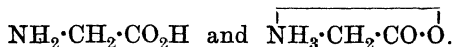
An unstable variety of glycine, differing from the ordinary one in crystalline form, has been described recently by H. King and A. D. Palmer.[12] Presumably this is the variety corresponding with the former of the above two formulæ, with a free carboxyl group, and it might be made to react with diazomethane. King and Palmer consider it probably identical with the fine needles which Emil Fischer obtained on precipitating an aqueous glycine solution with alcohol; it is the only variety of glycine that reacts with phosphorus pentachloride, which reaction also postulates a free carboxyl group. King and Palmer are mainly concerned with confirming the existence of compound of glycine with neutral salts,

[9] *Biochem. J.*, 1919, **13**, 378 ; *A.*, i, 338.
[10] *Zeitsch. physiol. Chem.*, 1914, **92**, 149 ; *A.*, 1914, i, 1057.
[11] *Biochem. Zeitsch.*, 1920, **105**, 111 ; *A*, i, 719.
[12] *Biochem. J.*, 1920, **14**, 576 ; *A*, i, 823.

described by Pfeiffer and his co-workers and called into question by Bayliss.

Hydroxyproline contains two asymmetric carbon atoms and in addition to the natural acid three stereoisomerides should exist. All have now been obtained by H. Leuchs and K. Bormann.[13] The puzzling transformation of tryptophan in the organism of the dog into kynurenic acid has now been almost certainly elucidated by A. Ellinger and Z. Matsuoka[14]; they synthesised indole-3-pyruvic acid and found that, like tryptophan, it is converted into kynurenic acid. The mechanism of the formation of this quinoline derivative would therefore presumably be as follows:—
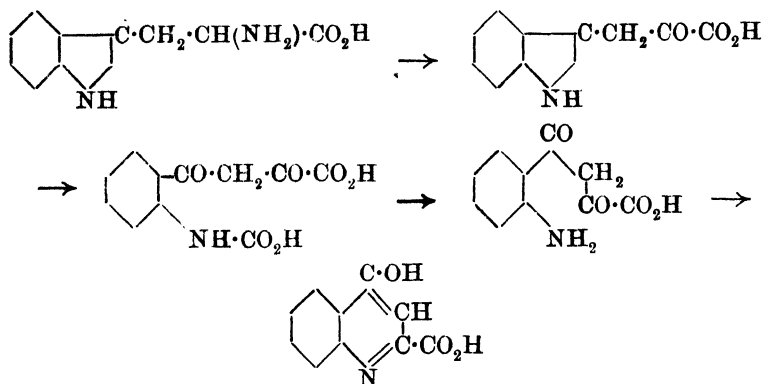
Here indolepyruvic acid figures as the first transformation product of tryptophan, which is in accordance with the known behaviour of other amino-acids.[15] As Ellinger and Matsuoka point out, the only criticism which can be urged is, that indolepyruvic acid is first transformed to tryptophan and that the amino-acid is converted into kynurenic acid by some other reaction, for it has been shown that, for instance, pyruvic acid itself may yield alanine, and phenylpyruvic acid phenylalanine, when perfused through the surviving liver. The hydroxyl group of kynurenic acid must be represented in its precursor, for quinoline-α-carboxylic acid is not oxidised to kynurenic acid in the dog, but is excreted partly unchanged, partly combined with glycine. The Hopkins-Cole test for tryptophan has been examined by W. R. Fearon[16] in a suggestive paper. Although the conclusions are based on

[13] Ber., 1919, 52, [B], 2086 ; A., i, 185.

[14] Zeitsch. physiol. Chem., 1920, 101, 259 ; A., i, 696.

[15] For example, F. Knoop and E. Kertess, ibid., 1911, 71, 252 ; A., 1911, ii, 514.   [16] Biochem. J., 1920, 14, 548 ; A., ii, 786.

molecular weight and nitrogen determinations only of amorphous pigments, and are therefore somewhat speculative, a considerable advance has been made, which ought to be useful in dealing with other substances (for example, alkaloids) related to tryptophan. Two molecules of indole, scatole, tryptophan or carbazole, were condensed with one molecule of an aldehyde (formaldehyde, glyoxylic acid, benzaldehyde) in *pure* glacial acetic acid by means of hydrogen chloride to leuco-compounds, which are oxidised to pigments, for example, for scatole.
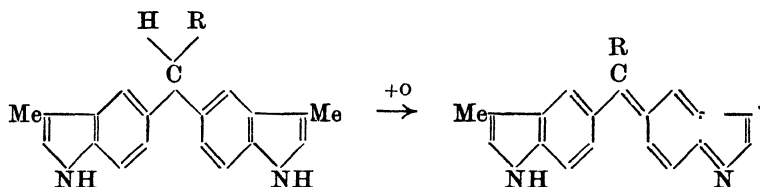
It will be seen that they are regarded as related to diphenyl-methane dyes. With tryptophan and formaldehyde or glyoxylic acid in the above-mentioned proportions the compounds are red, but with three molecules of the aldehyde to two of tryptophan blue compounds result, which are considered to arise from the condensation of the two additional aldehyde molecules with the two tryptophan side chains to form carboline derivatives of the type found in harman.[17] It is thus clear that blue compounds cannot be obtained from tryptophan combined as peptide, but red compounds might perhaps be expected in this case. As usually carried out, the Hopkins-Cole test results in a mixture of tryptophan red and blue.

Various colorimetric methods for estimating tryptophan have been examined by P. Thomas,[18] who prefers the use of *p*-dimethylaminobenzaldehyde as advocated by E. Herzfeld.[19] Thomas finds 1·7–1·8 per cent. in caseinogen, and as much as 2·3 per cent. in cerevisin, a protein from yeast, which is evidently able to form tryptophan from simpler compounds.

Similarly, L. Hugounenq and G. Florence[20] find that *Aspergillus* forms tryptophan when it has as only source of nitrogen any one of a series of natural amino-acids (it does not grow on phenyl-glycine). These authors also prefer *p*-dimethylaminobenzaldehyde for detecting tryptophan. The synthesis of tryptophan has also

[17] *Ann. Reports*, 1919, **16**, 156. W. H. Perkin and R. Robinson, *T.*, 1919. **115**, 967.

[18] *Bull. Soc. Chim. biol.*, 1914, **1**, 67 ; *A.*, i, 266.

[19] *Biochem. Zeitsch.*, 1913, **56**, 258 ; *A.*, 1913, ii, 1088.

[20] *Bull. Soc. Chim. biol.*, 1920, **2**, 13 ; *A.*, i, 466.

been investigated by W. J. Logie [21] in various bacteria, for example, *B. Coli*, which can form it from straight-chain compounds such as ammonium lactate and sodium aspartate, and also from free indole; the appearance of indole in some cultures may be attributed both to increased production and diminished consumption. The action of bacteria on amino-acids has been further studied in Japan by T. Sasaki [22] and his pupils. Thus K. Hirai [23] has found that *B. lactis aerogenes,* like yeast, forms tyrosol from *l*-tyrosine, but only in minute quantity. The same author [24] finds that a strain of *Proteus vulgaris,* capable of converting *l*-tyrosine into *d*-*p*-hydroxyphenyl-lactic acid, also converts histidine into *d*-β-iminazolyl-lactic acid. This new degradation of histidine should be compared with the production of urocanic (iminazolyl-acrylic) acid by bacilli of the *Coli* group, observed by H. Raistrick.[25] The curious difference in the stereo-chemical behaviour of *B. proteus* and *B. subtilis* originally observed by Sasaki for tyrosine, has been also demonstrated for *d*-*l*-phenylalanine by H. Amatsu and M. Tsudji.[26]

With Henderson's phosphate mixture phenyl-lactic acid and very little phenylethylamine is formed, *B. proteus* forming the dextro- and *B. subtilis* the laevo-variety of the acid. If instead of Henderson's mixture, uranyl phosphate and milk sugar are used as nutrient medium the amine is formed to the exclusion of the acid.

The Gases of the Blood.

This subject, more than any other, continues to occupy English physiologists, four out of the five papers in the current number of the *Journal of Physiology* are concerned with it. R. Wertheimer [27] has confirmed the observation hitherto only made accurately by R. A. Peters [28] that oxygen and hæmoglobin combine in molecular proportions as originally suggested by Hüfner. It should be noted, however, that Peters' values apply to hæmoglobin in the presence of dilute ammonia, and that Wertheimer only obtained agreement with these values in the presence of sodium carbonate; hæmoglobin dissolved in pure water had an oxygen

[21] *J. Path. Bact.,* 1920, **23**, 224 ; *A.,* i, 912.

[22] Compare *Ann. Reports,* 1917, **14**, 190, 191.

[23] *Acta Scholae Med. Univ. Kyoto,* 1918, **2**, 425 ; *A.,* i, 581.

[24] *Ibid.,* 1919, **3**, 49 ; *A.,* 1919, i, 612.

[25] *Ann. Reports,* 1917, **14**, 191 ; *A.,* 1917, i, 499 ; *Biochem. J.,* 1919, **13**, 446 ; *A.,* i, 348.

[26] *Acta Scholae Med. Univ. Kyoto,* 1918, **2**, 447 ; *A.,* i, 581.

[27] *Biochem. Zeitsch.,* 1920, **106**, 12 ; *A.,* i, 773.

[28] *J. Physiol.,* 1912, **44**, 131 ; *A.,* 1912, i, 519.

capacity 7 per cent. smaller. It is, however, the carbon dioxide in blood rather than the oxygen which stimulates work and controversy. We may first consider those authors who attempt to utilise the laws of mass action and of electrolytic dissociation to the full, without perhaps always considering sufficiently whether these laws apply to a colloidal solution like plasma or to a grossly heterogeneous system like whole blood.

T. R. Parsons[29] has attempted to calculate the carbon dioxide dissociation curve of blood on the assumption that a fixed amount of sodium is shared between two weak acids, namely, carbonic acid and hæmoglobin (with plasma proteins). The changes of reaction in blood due to increase of carbon dioxide pressure are much more gradual than in a sodium hydrogen carbonate solution because the proteins, and especially hæmoglobin, act as " buffers." Hæmoglobin would therefore have as important a function in carbon dioxide transport and maintenance of normal hydrogen ion concentration as in the transport of oxygen. The share of the plasma proteins (as distinct from hæmoglobin) in this buffer action is still a matter of dispute. If they act as buffers at all they must form ionised salts. A. R. Cushny[30] denies this; he filtered serum through collodion and found all the crystalloid constituents to be present in the same concentration in the filtrate as in the serum (with the exception of calcium and probably of magnesium). F. G. Hopkins,[31] on the other hand, evidently believes in the existence of ion-proteins. W. M. Bayliss[32] finds that the plasma proteins play no perceptible part in the maintenance of neutrality between limits of hydrogen ion concentration possible in the living organism. Parsons, in his second paper quoted above, considers that the weak acid competing with carbonic for the sodium is mainly, if not entirely, hæmoglobin. Using a similar conception, L. J. Henderson[33] has attempted to explain the simultaneous reaction of hæmoglobin with oxygen and with carbon dioxide. He is led to the assumption that a certain acid radicle of reduced hæmoglobin has a dissociation constant of $2 \cdot 3 \times 10^{-8}$, which is increased in oxyhæmoglobin to $2 \cdot 0 \times 10^{-7}$, thus expressing quantitatively an idea put forward by J. Christiansen, C. G. Douglas, and J. S. Haldane.[34] When the hæmoglobin thus becomes more electrolytically dissociated owing to its taking up oxygen, it also takes up

[29] J. Physiol., 1919, 53, 42, 340 ; A., i, 508.
[30] Ibid., 1920, 53, 391 ; A., i, 508.
[31] Brit. Med. J., 1920, ii, 70.
[32] J. Physiol., 1920, 53, 162 ; A., i, 507.
[33] J. Biol. Chem., 1920, 41, 401 ; A., i, 403.
[34] J. Physiol., 1914, 48, 244 ; A., 1914, i, 1012.

more-base (sodium) and carbonic acid is set free. (This would be the process in the lungs; the reverse would occur in the tissues.) It is impossible to do more here than indicate the fundamental notion of Henderson's paper.

In such theoretical speculations it is important to remember the observation made 30 years ago by Hamburger that red blood corpuscles are permeable to chloride and phosphate ions; his pupil S. de Boer [35] more recently showed the same to be the case for sulphate ions. This ionic interchange between plasma and corpuscles has lately attracted the attention of a number of workers. L. S. Fridericia [36] finds that the increased chlorine content of the corpuscle can be demonstrated at low pressures of carbon dioxide in the plasma, for example, 0·1 atmosphere. The amount of chlorine gained by the corpuscles on increasing the carbon dioxide pressure from 0·08 to 162 mm. almost completely accounts for the increased carbon dioxide-combining power coincidently gained by the plasma. The hydrogen ion concentrations of plasma and corpuscles remain fairly constant. This is an extension of K. A. Hasselbalch's [37] attempt to explain that whereas a sodium hydrogen carbonate solution contains the same amount of carbon dioxide at all (except very low) pressures of · the gas, in blood, on the other hand, the carbon dioxide-combining power increases with the pressure (as if bicarbonate had been added). Hasselbalch invokes the ampholyte character of hæmoglobin, which he conceives as having an acid character at low carbon dioxide pressures so that it displaces carbon dioxide from bicarbonate, and alkaline qualities at high carbon dioxide pressures, so that it combines with increasing amounts of carbon dioxide. The obvious question remained, how can hæmoglobin in the corpuscles influence bicarbonate in the plasma? Fridericia insists that the necessary link between the two phases is to be found in the wandering of the anions. H Straub and K. Meier [38] have approached the same question by subjecting corpuscles in physiological saline to various concentrations of carbon dioxide. The corpuscles themselves act as buffers, their P_H being 7·00 when that of the solution was 6·67. The authors connect this effect with the partial permeability and the colloidal properties of the corpuscles. Their work has been discussed by L. Michaelis.[39] Working on somewhat similar lines, J. M. H. Campbell and E. P.

[35] *J. Physiol.*, 1917, **51**, 211 ; *A.*, 1917, i, 671.

[36] *J. Biol. Chem.*, 1920, **42**, 245 ; *A.*, i, 648.

[37] *Biochem. Zeitsch.*, 1916, **78**, 112 ; *A.*, 1917, i, 490.

[38] *Ibid.*, 1918, **89**, 156 ; **90**, 305 ; 1919, **98**, 205, 228. *A.*, 1918, ii, 467 ; 1919, i, 53 ; 1920, i, 200.   [39] *Ibid.*, 1920, **103**, 53 ; *A.*, i, 579.

Poulton[40] also find the isoelectric point of hæmoglobin at P_H 6·98 Under physiological conditions the blood proteins act as acids and do not themselves combine with carbon dioxide until the blood is much more acid than ever happens in the body. The partition of carbon dioxide between corpuscles and plasma at different carbon dioxide pressures has also been recently investigated by J. Joffe and E. P. Poulton[41] with results similar to those of Straub and Meier. The former authors criticise D. D. van Slyke and G. E. Cullen's method,[42] for the determination of the alkali reserve, because the venous plasma, *after the separation of the corpuscles*, is brought into equilibrium with alveolar carbon dioxide, so that an ionic interchange with the corpuscles can no longer take place.

In most of the above papers carbon dioxide is not considered to be combined with the blood proteins, but to be entirely present as bicarbonate (at least under physiological conditions). This view is opposed by G. A. Buckmaster,[43] who revived Bohr's conception of a direct combination between carbon dioxide and hæmoglobin. A third view has recently been put forward by J. Mellanby and C. J. Thomas[44] in a paper which contains some novel experiments and views running counter to the current conception. These authors studied more particularly the ash associated with the blood proteins under various conditions. For instance, the protein precipitated from serum by adding an equal volume of alcohol at $-10°$ is associated with a large amount of inorganic salt. When redissolved in water this protein combines with more carbon dioxide than can be calculated as existing in combination with the alkaline salt; from this and other experiments Mellanby and Thomas conclude that the carbon dioxide is adsorbed, chiefly on the fibrinogen, and that the proteins effect the transport of carbon dioxide. Since a 0·2 per cent. solution of sodium hydrogen carbonate is not precipitated by an equal volume of alcohol at $-10°$, it is incidentally concluded that this salt does not exist free in serum. The authors consider the bicarbonate hypothesis inadmissible (according to which the sodium is shared between carbonic and another weak acid). Sodium hydrogen carbonate with protein constitutes the alkali reserve. In shed blood lactic acid is produced from the corpuscles and that is why the carbon dioxide of shed blood falls steadily, and why this gas can be extracted completely from ·blood in a vacuum, but not from serum.

It seems to the writer that if the bicarbonate is adsorbed by the

[40] *J. Physiol.*, 1920, **54**, 152.   [41] *Ibid.*, 129.
[42] *Ann. Reports*, 1917, **14**, 173.   [43] *Ibid.*, 1918, **15**, 147.
[44] *J. Physiol.*, 1920, **54**, 178.

serum proteins, the latter still may transport carbon dioxide as salt, in accordance with the view more generally accepted. Mellanby and Thomas lay great stress on the colloidal properties of serum and support the doubt, expressed above, that the laws of equilibrium in homogeneous systems are not immediately applicable to this case. •

The estimation of carbon monoxide in blood and of the latter's CO-capacity has been described by M. Nicloux.[45]

An interesting contribution to the technique of determining the hydrogen-ion concentration of blood has been made by H. H. Dale and C. L. Evans.[46] They dialyse about 5 c.c. of oxalated blood into 1 c.c. of saline, avoiding loss of carbon dioxide. The P_H of the dialysate is then found colorimetrically, by mixing phosphate solutions until the mixture gives with neutral-red the same colour as the dialysate. The method appears to be very convenient and accurate, and may well be applicable to fluids other than blood. The regulation of the blood's alkalinity has been investigated by H. W. Davies, J. B. S. Haldane, and E. L. Kennaway,[47] who find at high carbon dioxide-pressures a considerable deviation from Parsons' theoretical dissociation curve, referred to above. They studied the effect of eating large quantities of sodium hydrogen carbonate, which produces increased carbon dioxide-capacity of the blood, increase in alveolar carbon dioxide, rapid excretion of bicarbonate in the urine, disappearance or great decrease of urinary ammonia and sometimes appearance of acetone substances. These effects illustrate the way in which the organism compensates for alkalosis by changed respiration and metabolism. The ammonia normally excreted in the urine would ultimately appear as neutral urea and the acid normally combined with it becomes available for neutralising the alkali ingested. For the related subject of acidosis reference can here only be made to papers by H. W. Haggard and Y. Henderson.[48]

Accessory Food Substances.

The name vitamines is all but established, in spite of the fact that it suggests a relationship to amines, of which there is no proof. J. C. Drummond[49] suggests a compromise by dropping the final " e," so as not to suggest basic properties (to those familiar with the Chemical Society's nomenclature). He further calls fat-soluble-*A*

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[45] *Bull. Soc. Chim. biol.*, 1920, **2**, 171.
[46] *J. Physiol.*, 1920, **54**, 167.   [47] *Ibid.*, 32.
[48] *J. Biol. Chem.*, 1920, **43**, 3, 15.
[49] *Biochem. J.*, 1920, **14**, 660 ; *A.*, i, 908.

and water-soluble-B, simply vitamin-A, vitamin-B, etc. Work on accessory food substances is going on with unabated vigour in England and in America; there are also signs of increased interest in and recognition of the subject in France and in Germany. On account of its great value, we may once more refer here to the Special Report No. 38 of the Medical Research Committee (now Research Council), which survey was mentioned in last year's Report.

It seems that the resistance of some accessory food factors to high temperatures has been somewhat underestimated. Thus H. Steenbock and P. W. Boutwell[50] now report that the fat-soluble vitamin-A of yellow maize is unaffected by heating for three hours under 7 kilos pressure, nor does this treatment appreciably diminish the same factor in chard, carrots, sweet potatoes and squash. The relative stability of vitamin-A is also insisted on by T. B. Osborne, L. B. Mendel and A. J. Wakeman,[51] who cannot confirm the great thermolability formerly attributed to this substance from animal sources by H. Steenbock, P. W. Boutwell and H. E. Kent,[52] and by J. C. Drummond.[53] The explanation of this discrepancy is probably found in an experiment described by F. G. Hopkins[54] in opening a discussion on vitamins in clinical medicine at the annual meeting of the British Medical Association last July. Butter fat heated for four hours to 120° without aeration remains active, but when a stream of air is bubbled through it during the heating, it becomes inactive. It seems that the fat-soluble vitamin possesses considerable heat-stability but is easily oxidised. That vitamins are readily destroyed by oxidation seems also to result from the fact, related by A. F. Hess,[55] that milk or neutralised canned tomato juice loses much of its activity by being shaken with air for half an hour. The deleterious effect sometimes observed in pasteurised milk may be the result of exposure to warm air rather than a simple temperature effect. G. F. Still[56] points out that so-called "buddized milk," sterilised by being warmed with hydrogen peroxide to 50°, was found clinically to have lost its anti-scorbutic properties. Laboratory experiments on the effect of suitable oxidising agents on the various vitamins at room temperature now seem desirable. Similarly, E. M. Delf[57] finds that the anti-scorbutic vitamin-C of orange and swede juice has

[50] J. Biol. Chem., 1920, **41**, 163 ; A., i, 358.
[51] Ibid., 549 ; A., i, 457.
[52] J. Biochem., 1918, **35**, 517 ; A., 1918, i, 513.
[53] Biochem. J., 1919, **13**, 81 ; A., 1919, i, 363.
[54] Brit. Med. J., 1920, ii, 147.
[55] Ibid., ii, 154.   [56] Ibid., ii, 156.
[57] Biochem. J., 1920, **14**, 211 ; A., i, 460.

an unexpectedly great stability above 100° if the heating is conducted in the absence of air. The practical bearing of these experiments on canning and other methods of food-preservation is obvious and the same applies to those of A. Harden and R. Robison,[58] who find that with suitable precautions orange juice may be evaporated to dryness without loss of activity and that the dry residue retains much of its activity after two years' storage.

A few further attempts have been made to isolate the water-soluble antineuritic vitamin-B, which for various reasons seems to hold out more hope than vitamins-A or -C. The most interesting of these attempts is that made by F. Hofmeister and M. Tanaka,[59] who during the war isolated from rice polishings a base *oridine*, $C_5H_{11}O_2N$, which as crude hydrochloride cured polyneuritis of pigeons in small doses, but became inert when purified for analysis. Either the antineuritic vitamin was a mere impurity in the crude crystals and therefore extraordinarily active, or the active substance underwent chemical transformation during the process of purification (regeneration from aurichloride and recrystallisation of the hydrochloride so obtained). Although the empirical formula of oridine is the same as that of valine, the substance appears to be more closely related to pyridine and is possibly a dihydroxypiperidine. The result reminds one of C. Funk's earlier investigations when the antineuritic substance was associated with nicotinic acid. C. N. Myers and C. Voegtlin,[60] using methods for the isolation of bases somewhat similar to those employed by Funk, obtained from dried yeast a crystalline antineuritic substance which became inactive on drying. The method of extracting vitamin-B from rice bran has been studied by B. C. P. Jansen,[61] who states that an alcoholic extract of rice polishings is now used in Java against beri-beri. He used 0·3 per cent. aqueous hydrochloric acid, or 70 per cent. alcohol, or 96 per cent. alcohol with $\frac{1}{15}$ volume of concentrated hydrochloric acid, and found that with each solvent the vitamin is completely extracted in two days. He criticises curative experiments with pigeons as being uncertain unless much time is expended on them; it is better, and not necessarily slower, to find the minimum preventive dose which must be added to a diet of polished rice. Much time may be saved by using a small species of Indian bird (*Musica maja*), which is far more sensitive than the pigeon.

The results obtained in the laboratory with animals are now

[58] *Biochem. J.*, 1920, **14**, 171 ; *A.*, i, 460.
[59] *Biochem. Zeitsch.*, 1920, **103**, 218 ; *A., i*, 586.
[60] *J. Biol. Chem.*, 1920, **42**, 199 ; *A.*, i, 500.
[61] *Mededeelingen Geneesk. Lab. Weltevreden*, 1920, [iii], A, 23.

more and more being put to clinical use, most of all in Vienna.[62]
Charts [63] giving the effect of butter or cod liver oil and fresh turnip
juice, added to the diet of nursing mothers or of infants, demon-
strate the same remarkable effect on the body weight of the chil-
dren as has been studied in animals. Turnip juice contains the
antiscorbutic vitamin and is a cheap substitute for lemon juice;
its clinical value has now also been emphasised in Germany.[64]
Various gastro-intestinal disorders in adults are now attributed by
R. McCarrison [65] to vitamin deficiency and he has found, for in-
stance, that healthy monkeys, carriers of *Entamœba* cysts, develop
dysentery when placed on devitaminised food.

Evidence is accumulating that vitamins are not only necessary
for animals, but also for some fungi. R. J. Williams,[66] F. M.
Bachmann,[67] W. H. Eddy, and H. C. Stevenson [68] estimate the
strength of vitamin (*B* ?) solutions by growing yeast cells in them.
In his second paper Williams has made the method gravimetric
by weighing the yeast. The method has been adversely criticised
by G. de P. Souza and E. V. McCollum,[69] who find that many
substances stimulate the growth of yeast. Pasteur already failed
to grow yeast from a single cell in synthetic media, and Wildier [70]
postulated a special substance, " bios," necessary for the growth
of yeast cells. A similar relationship seems to hold for *Sclerotinia
cinerea*, the fungus causing brown rot in peaches and plums; ac-
cording to J. J. Willaman,[71] it does not grow on synthetic media
sufficing for *Aspergillus*, for example, but it will grow when a
" vitamin " preparation is added, obtained by means of adsorption
by fullers' earth from a variety of animal and vegetable sources.
This substance, like " bios," is thought to be identical with water-
soluble vitamin-*B*, but such a speculation is of course incapable of
exact verification as long as vitamins have not been isolated.
Indeed, the identity of the growth-promoting water-soluble vitamin
with the antineuritic, now generally presumed, is denied by A. D.
Emmett in conjunction with G. O. Luros [72] and with M. Stock-
holm.[73] That vitamins are necessary for fungi is also denied; A.
Lumière [73a] finds that yeast heated to 135° and no longer capable

[62] (Miss) H. Chick, *Brit. Med. J.*, 1920, ii, 131. [63] E. J. Dalyell, *ibid.*, ii, 132.
[64] H. Aron and S. Samelson, *Deutsch. med. Woch.*, 1920, 46, 772.
[65] *Brit. Med. J.*, 1920, i, 822.
[66] *J. Biol. Chem.*, 1919, 38, 465 ; 1920, 42, 59 ; *A.*, 1919, i, 463.
[67] *Ibid.*, 1919, 39, 235 ; *A.*, 1919, i, 613.
[68] *Ibid.*, 1920, 43, 295 ; *A.*, ii, 716.
[69] *Ibid.*, 1920, 44, 113 ; *A.*, i, 919.   [70] *La cellule*, 1901, 18, 313.
[71] *J. Amer. Chem. Soc.*, 1920, 42, 549 ; *A.*, i, 412.
[72] *J. Biol. Chem.*, 1920, 43, 265 ; *A.*, i, 698.
[73] *Ibid.*, 287 ; *A.*, i, 701.   [73a] *Compt. rend.*, 1920, 171, 271 ; *A.*, i, 653.

of curing polyneuritis gives a bouillon which greatly improves the development of fungi. From what has been said above it will be seen that Lumière's experiments are not necessarily in conflict with those of Williams and of Bachmann. Heating to 135° may not have left enough vitamin to cure pigeons; yet there might be enough to have a favourable effect on the growth of yeast. It is even more difficult to judge of the vitamin-nature of the crude nucleic acid derivatives in bacterised peat, which according to W. B. Bottomley [74] favour the growth of *Lemna* in water culture. Experiments on the growth-promoting substances in various organic manurial composts by F. A. Mockeridge [75] seem to depend more definitely on the presence of purine and pyrimidine bases in these manures.

Pellagra, a disease occurring in countries (Italy, Carolina) where maize is the principal article of diet, has of late years been more and more considered due to a dietary deficiency, and it has been suggested that the cause lies in the absence of tryptophan and perhaps also of lysine from zein, the chief protein of maize. The metabolic importance of the former amino-acid was established by E. G. Willcock and F. G. Hopkins [76] in the case of young mice, that of the latter by T. B. Osborne and L. B. Mendel. [77]

Occasional outbreaks of pellagra in institutions, camps, etc., have always cleared up on the inclusion of more milk, meat, eggs or cheese in the dietary, but whether the cure was due to tryptophan in caseinogen is not thoroughly established. H. Chick and E. M. Hume [78] describe experiments with monkeys on a diet rich in all known vitamins, but with zein as its principal protein. Symptoms closely resembling those of pellagra were produced and were undoubtedly of dietary origin. In one case they cleared up rapidly when caseinogen was administered as well, but the crucial point, whether it was tryptophan which made the difference, could not be established with certainty. This amino-acid appeared to have a beneficial effect, but no cure was effected with it alone.

Ferments.

The discussion on the diastase-like properties of formaldehyde, which has been carried on in Germany during the last few years, may be mentioned here, not so much as a contribution to our know-

[74] *Proc. Roy. Soc.*, 1920, [B], **91**, 83 ; *A.*, i, 265.
[75] *Biochem. J.*, 1920, **14**, 432 ; *A.*, i, 704.
[76] *J. Physiol.*, 1906, **35**, 88 ; *A.*, 1907, ii, 88.
[77] *J. Biol. Chem.*, 1914, **17**, 325 ; *A.*, 1914, i, 620.
[78] *Biochem. J.*, 1920, **14**, 135.

ledge of enzymes, but rather as a curious example of scientific·
controversy. G. Woker and H. Maggi have repeatedly asserted,
both separately and together,[79] that formaldehyde has the power of
hydrolysing starch. They have been attacked by various critics
in a number of separate papers, and finally these critics have
banded themselves together in a final onslaught.[80] The explana-
tion of the supposed diastatic action of formaldehyde lies in the
fact that the latter forms a loose additive compound with starch
(which compound does not give a blue colour with iodine), and
that formaldehyde also modifies the physical properties of the
colloid. This view is shared by E. Herzfeld and R. Klinger,[81]
who hold similar views as to the action of formaldehyde and for-
mulate, in addition, somewhat revolutionary ideas on starch hydro-
lysis, according to which the formation of dextrins (including
achroodextrins) may be a purely physical change in the degree
of dispersion, without any hydrolysis. The hydrolysis of starch
(by amylase) is also discussed in a suggestive, largely theoretical
paper by L. Ambard, E. Pelbois and M. Bricka,[82] who consider
it to be just as much a unimolecular reaction as the hydrolysis of
sucrose by acids. The action of neutral salts is similar, accelerat-
ing the latter, and making possible the former action (dialysed
saliva is without action on starch). In either case the action of
the neutral salt is on the *substrate*, not on the catalyst. For starch
the action depends on the anion and is greatest for chlorides, at
P_H 6·45, which gives also the reaction of a solution in which the
amylase is most stable. Under these conditions the optimum con-
centration of sodium chloride is 0·006 molar, but in this neigh-
bourhood considerable changes in the salt concentration do not
very much affect the rate of hydrolysis.

Potato tyrosinase has been separated by H. Haehn[83] into two
components by means of a Bechhold ultra-filter. The residue is
thermolabile "α-tyrosinase," the filtrate is an "activator" which
retains its activity after incineration. In the case of a successful
separation (which is not always possible), the two components are
separately inactive on tyrosine, but become so when mixed.

It is natural that attempts have been made to demonstrate the
reversibility of hydrolytic action in such a simple and specific case
as that of urease, and H. P. Barendrecht,[84] in developing a radia-

[79] For example, *Ber.*, 1919, **52**, [B], 1594 ; *A.*, i, 10.

[80] M. Jacoby, W. von Kaufmann, A. Lewite, and H. Sallinger, *ibid.*, 1920,
53, [B], 681 ; *A.*, i, 424.   [81] *Biochem. Zeitsch.*, 1920, **107**, 268 ; *A.*, i, 713.

[82] *Bull. Soc. Chim. biol.*, 1920, **2**, 42.

[83] *Ber.*, 1919, **52**, [B], 2029 ; *A.*, i, 102 ; *Biochem. Zeitsch.*, 1920, **105**, 169 ;
A., i, 777.

[84] *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 29, 126 ; *A.*, i, 102, 195.

tion theory of enzyme actions, claims that urease under certain conditions can transform ammonium carbonate into urea. This is denied by T. J. F. Mattaar.[85] In any case urease undergoes more or less rapid destruction in a solution of ammonium carbonate.

E. Yamasaki[86] has investigated the kinetics of urease and considers that the hydrolysis of urea is a simple catalytic action carried on in the substrate phase and does not consist in the decomposition with measurable velocity of an intermediate compound formed instantaneously. Nor do the enzyme and substrate form an intermediate compound with measurable velocity. The addition of electrolytes diminishes the activity of the enzyme owing to adsorption by the latter, and the effect may in various cases be expressed according to Freundlich's adsorption formula. Perhaps it is the electrolyte nature of ammonium carbonate which prevents the reversibility of the urease action from being demonstrated.

The same author[87] has compared the temperature-coefficients for the destruction of catalase from bamboo shoots, germinated soja beans and blood. As the coefficient is different in each case, he concludes that the enzymes are also different. The effect of "poisons" is considered to be due to adsorption by and coagulation of the enzyme. C. G. Santesson[88] also considers that the effect of electrolytes on the rate of the catalase action is due to adsorption and finds that the anions can be arranged in Hofmeister's lyotropic series, SO_4 having the smallest and CN the greatest inhibitory effect. C. Neuberg and F. F. Nord[89] have extended the reduction, by yeast, of the carbonyl group from aldehydes to ketones. In the latter case they get *optically active* secondary alcohols in yields of about 10 per cent. Diacetyl yields *l*-$\beta\gamma$-butylene glycol, whereas Harden and Walpole found that bacteria produce from carbohydrates a mixture of the racemic and meso-forms. Another interesting product of ferment action is the crystalline specimen of sucrose obtained by E. Bourquelot and M. Bridel,[90] by the action of emulsin on gentianose. Previously this trisaccharide had only been hydrolysed to fructose and gentiobiose by invertase, and then the latter sugar could be split into two molecules of dextrose by "gentiobiase" of bitter almonds. The authors were, however, led to attempt a different degradation by the simultaneous occurrence of sucrose and gentiobiose in fresh

[85] *Rec. trav. chim.*, 1920, **39**, 495 ; *A.*, i, 649.

[86] *Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 97 ; *A.*, i, 577.

[87] *Ibid.*, 1920, **9**, 13, 59, 75, 89 ; *A.*, i, 194, 453, 574, 576.

[88] *Skand. Arch. Physiol.*, 1920, **39**, 236 ; *A.*, i, 576.

[89] *Ber.*, 1919, **52**, [B], 2237, 2248 ; *A.*, i, 135.

[90] *Bull. Soc. Chim. biol.*, 1920, **2**, 160 ; *Compt. rend.*, 1920, **171**, 11 ; *A.*, i, 530.

gentian root. They finally succeeded by using a specimen of bitter almonds as free as possible from invertase, and controlling the length of the reaction polarimetrically.

Estimation and Formation of Urea.

Hypobromite does not liberate the whole of the nitrogen from urea and the addition of substances like dextrose has been shown by M. Krogh[91] to give illusory results, since carbon monoxide is given off. L. Ambard[92] now criticises Krogh's high results because oxygen is also evolved. After absorption of this gas by sodium hyposulphite the nitrogen corresponds with 90 per cent. of the theoretical. Apart from the use of urease, a more elegant method of estimating urea is that given by R. Fosse,[93] which does not appear to have received in this country the attention it deserves. It is based on the fact that xanthhydrol precipitates urea at dilutions as high as 1:1,000,000. The method has been recently critically examined and favourably reported on by Frenkel.[94] With its aid Fosse has lately studied the formation of urea by oxidising proteins with permanganate, first observed by Béchamp in 1856, but afterwards denied. Ordinarily only small amounts are produced, but if the oxidised solution is subsequently heated with ammonium chloride, much larger quantities of urea result,[95] because the solution contains cyanic acid.[96] When dextrose is added during oxidation the yield of urea is also much increased and small quantities of dextrose alone, in the presence of concentrated ammonium hydroxide, may yield 70 per cent. of the sugar as urea.[97] The reaction is considered to proceed through the stages: formaldehyde, hydrocyanic acid, cyanic acid, ammonium cyanate, and it is suggested that this explains the formation of urea in plants. Under certain conditions a little oxamide may also be formed.[98]

[91] *Zeitsch. physiol. Chem.*, 1913, **84**, 379 ; *A.*, 1913, ii, 641.

[92] *Bull. Soc. Chim. biol.*, 1920, **2**, 205 ; *A.*, 1921.

[93] *Compt. rend.*, 1914, **158**, 1076, 1588 ; **159**, 250 ; *A.*, 1914, ii, 506, **593**, 756 ; *Ann. Reports*, 1914, **11**, 178.

[94] *Ann. Chim. anal.*, 1920, [ii], **2**, 234 ; *A.*, ii, 646. Compare also P. Carnot, P. Gérard and S. Moissonnier, *Compt. rend Soc. Biol.*, 1919, **82**, 1136 ; M. Laudat, *ibid.*, 1920, **83**, 730 ; *A.*, ii, 645 ; W. Mestrezat and M. Janet, *ibid.*, 1920, **83**, 763 ; *A.*, ii, 645, 779.

[95] *Compt. rend.*, 1919, **168**, 320 ; *A.*, 1919, i, 152.

[96] *Ibid.*, 1919, **169**, 91 ; *A.*, 1919, i, 459.

[97] *Ibid.*, 1919, **168**. 1164 ; *A.*, 1919, i, 313.

[98] *Compt. rend.*, 1920, **171**, 398 ; *A.*, i, 664.

Hormones.

During the current year several attempts have been made to isolate the physiologically active principles of the pituitary body, but the position seems to be rather less hopeful than last year when J. J. Abel and S. Kubota [99] suggested that the plain muscle stimulant of pituitary might be identical with histamine. This suggestion was promptly rejected by D. Cow [1] and at once reaffirmed by J. J. Abel and D. I. Macht.[2] The attack and defence were made on purely pharmacological grounds, and may be cited as an illustration of the difficulties involved in settling the identity or non-identity of substances exclusively by their physiological action, without the chemical isolation of both. The differences in the physiological behaviour of the two substances, used by Cow in support of his argument, were considered by Abel and Macht to be the result of differences in dosage. The notion that the pituitary uterine stimulant (oxytocic principle) is merely histamine was also rejected on more chemical evidence by H. W. Dudley,[3] who extracted the dry powdered gland with acidulated water and purified the extract with colloidal ferric hydroxide, which leaves the active principle entirely in solution. It can then be removed completely without loss by continuous extraction with butyl alcohol (under reduced pressure, so as to lower the temperature). The substance from pituitary is not identical with histamine, because, unlike this amine, it is destroyed at room temperature by N-sodium hydroxide, and further, because it is destroyed by trypsin, is extracted from *acid* solution by butyl alcohol, and is insoluble in boiling chloroform. As the result of Dudley's experiments and later ones of their own, J. J. Abel and T. Nagayama [4] have had to abandon the hope that the pituitary uterine stimulant is histamine. They nevertheless claim that infundibular extracts from fresh glands contain a little histamine, but much less than extracts of commercial dried gland previously examined by them, or than the extracts commonly employed in therapeutics. They suggest that the specific active principle, on boiling and sterilisation, partly breaks down to histamine. The fact that they obtained an impure substance which is many times more oxytocic than histamine itself, is in itself sufficient to dispose of their previous suggestion that the two are identical. It also makes the chances of isolation much smaller—evidently this pituitary prin-

[99] *Ann. Reports*, 1919, **16**, 158.   [1] *J. Pharm. Expt. Ther.*, 1919, **14**, 275.
[2] *Ibid.*, 279.   [3] *Ibid.*, 295; *A.*, i, 344.
[4] *Ibid.*, 1920, **15**, 347.

ciple is a substance of quite extraordinary potency and present in very small amount.

M. T. Hanke and K. K. Koessler[5] go further than Abel and Nagayama, and deny that histamine is present at all in fresh pituitary; they partly rely on a colorimetric method for estimating histamine,[5a] and they incidentally cite a number of chemical and physiological differences between the amine and the pituitary principle. With regard to the latter, F. Fenger and M. Hull[6] state that in the fresh gland it is united to a protein complex and is insoluble in 95 per cent. alcohol, which, however, on boiling splits off a highly active, hygroscopic substance, more readily decomposed than its precursor. Of late most writers, for instance, Dudley[8] and C. Crawford,[7] consider the uterine and the pressor principle of pituitary to be distinct. According to the latter, the pressor principle gives no Millon reaction and only a very doubtful Pauly reaction, but on keeping an aqueous solution it becomes reactive to Pauly's reagent. Abel and Macht find that the Pauly reaction is always given by active preparations. In spite of the great therapeutical importance of the pituitary, the prospects of isolating any specific active principle from it do not appear to be very bright.

L. Stern and E. Rothlin[8] have prepared an impure substance from the spleen which they call "liénine"; it acts on smooth muscle very much like histamine, and has some of the chemical properties of the latter substance. The chief difference appears to be that liénine is destroyed by 1 per cent. sodium hydroxide, and histamine is not. Of a number of organ extracts examined as regards their action on smooth muscle fibre, that of the spleen is by far the most potent and the active substance is stated to be present in the blood of the splenic vein. Further chemical work is required to prove or disprove its identity with histamine.

Thyroxine was referred to at some length in last year's Report. Since then a long paper by E. C. Kendall and A. E. Osterberg[9] has come to hand, containing numerous microphotographs of crystals. Many analyses of thyroxine and its derivatives are now given for the first time, and the conditions governing the transformation of the ketonic or lactam into the enolic or lactim form and into the open chain hydrate are discussed. It is stated that the position of the three iodine atoms is determined by

[5] *J. Biol. Chem.*, 1920, **43**, 557.   [5a] *Ibid.*, 543; *A.*, 784.
[6] *Ibid.*, 1920, **42**, 153.
[7] *J. Pharm Expt. Ther.*, 1920, **15**, 81 ; *A.*, i, 458.
[8] *J. Physiol. Path. gén.*, 1920, **18**, 753 ; *A.*, i, 649.
[9] *J. Biol. Chem.*, 1919, **40**, 265 ; *A* , i, 180.

synthesis, a description of which is promised later. Meanwhile E. C. Kendall has further developed the estimation of iodine in the thyroid; he thinks it best to use only 0·5 gram of the gland. E. C. Kendall and F. S. Richardson [10] find that there is 0·013 mg. of iodine in 100 c.c. of normal blood.

GEORGE BARGER.

[10] *J. Biol. Chem.*, 1920, **43**, 161 : *A.*, ii, 631. Compare also S. B. Kuzirian, *Proc. Iowa Acad. Sci.*, 1918, **25**, 495 ; *A.*, ii, 445.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

MUCH steady progress has to be reported, although no development of outstanding importance has occurred.

The outlook for the future is in some directions rather uncertain. The Woburn Fruit Farm, long carried on at the expense of the Duke of Bedford, and made famous by the important investigations of the late Spencer U. Pickering, will be closed before this Report appears; and at the moment of writing there is the possibility that the Woburn Experimental Station of the Royal Agricultural Society may be closed in 1921, although some hope still remains that this misfortune may be mitigated, or even averted. It seems probable that the research in agricultural science done by Germany and Austria will be less in future than it was before the War. As against that, however, the Ministry of Agriculture in this country has produced an admirable scheme, whereby the research institutes can attract the ablest of the younger men and women from the universities, and it may safely be said that the institutes were never before as well staffed as they are now. Both in amount and quality, the work in hand at the various centres of agricultural research in this country is full of promise for the future. Fortunately, also, in spite of the centralisation which is being forced by inexorable circumstances, there still remain independent outside critics who can save the workers at the institutes from the dangers of futility.

Soil.

It seems possible that the nature of the black organic matter in the soil, commonly known as "humus," will soon be understood.

Humus is formed from cellulose in the soil; no great amount seems to be obtained from the protein in plant residues. Maillard showed some years ago that a substance resembling humus is produced when sugar is heated either with mineral or amino-acids; in the latter case, the "humus" contains nitrogen, as in soil.

The reaction has been further investigated by V. A. Beckley in the Rothamsted laboratories;[1] setting out from an observation by Fenton, he showed that sugars, on treatment with acids, give rise to hydroxymethylfurfuraldehyde, which readily condenses to form a substance closely resembling humus. He also found indications of the presence of hydroxymethylfurfuraldehyde in a dunged soil and in rotting straw in which humus was being produced. He suggests, therefore, that the formation of humus in soil proceeds in two stages:

Carbohydrate (cellulose, etc.) + amino-acid =
$$\text{hydroxymethylfurfuraldehyde.}$$
Hydroxymethylfurfuraldehyde + amino-acid =
$$\text{humus} + \text{furfuraldehyde} + CO_2 \text{ by condensation.}$$

An alternative view is put forward that humus is derived from the oxidation of quinones.[2]

The humus has acid properties, which, however, are very difficult to measure. An interesting series of papers has been published[3] by S. Odén, of Upsala, one of the most ingenious of present-day workers on this difficult subject. He shows that selective absorption, once invoked to account for the acidity, can really play but a very minor part, since treatment of washed peat with potassium chloride solution gives no hydrochloric acid, but only non-volatile acids. Nor did iron or aluminium occur in the solution. Humic acid is a true acid;[4] it appeared, however, from the high P_H value of peat extracts that other organic acids were present as well. A method is described for obtaining neutralisation curves which will probably prove distinctly helpful to investigators.

He further discusses the effect of lime on peat.[5] It is well known that large quantities of lime—one or two tons per acre—are necessary in order to allow of the growth of agricultural crops on peat soils; whilst on normal soils much smaller quantities suffice. The usual explanation is that peat contains some harmful substance put out of action by lime. Odén shows that humic acid is so insoluble that it can hardly do much harm to vegetation; he also controverts Baumann and Gully's view that injury arises by absorptive decomposition of nutritive salts with liberation of acid. Further, he demonstrates by the old van Bemmelen method that lime effects no improvement in the fundamental water relation-

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[1] *J. Agric. Sci.*, 1920, **11**, 69.

[2] W. Eller and K. Koch, *Ber.*, 1920, **53**, [B], 1469; *A.*, i, 733.

[3] *Int. Mitt. Bodenk.*, 1920, 9, 361; he has also published a monograph dealing with the whole question of humus: *Koll. Chem. Beihefte*, 1919, **10**, 75.

[4] For further confirmation, see F. Fuchs, *Chem. Zeit.*, 1920, **44**, 551; *A.*, i, 596.   [5] *Int. Mitt. Bodenk.*, 1920, **9**, 375.

ships of peat. He concludes that humic acid is not itself harmful to plants, but, on the other hand, the calcium humate formed when lime is added to peat is distinctly beneficial, probably by acting as a "buffer" in regulating the hydrogen-ion concentration of the soil. It would react with harmful acids, forming harmless calcium salts and insoluble, harmless humic acid, thus maintaining the soil reaction suitable for plants and micro-organisms.

He also describes a colorimetric method for estimating the amount of humic acid in soil.[6] The problem is complicated by the fact that two intensely dark-coloured substances occur, namely, humic acid and the so-called hymatomelanic acid, in addition to the faintly coloured acids formerly known as crenic and *apo*crenic acids, but named "fulvic" by Odén.[7]

As separation of the two dark-coloured acids is not easy, a detailed examination was made of the absorption spectra of their sodium salts as well as of that of Merck's "acidum huminicum"; from the curves and data thus obtained the details of the method are worked out.

An aqueous extract of peat undergoes considerable changes on keeping, which have been examined in some detail.[8]

The organic phosphorus compounds of the soil have been studied in Ohio.[9] About one-third of the total phosphorus in the surface soil and one-fifth of that in the subsoil is found to be in this form, and this organic phosphorus is related both to the "humus soluble in ammonia," of which it forms about 1 per cent., and to the total nitrogen, being one-tenth the amount of the latter. There was no evidence that the organic phosphorus compounds have much direct nutrient value to plants, although they apparently undergo decomposition, since the amount in virgin soil is considerably above that in cultivated soil containing approximately the same quantity of total phosphorus.

The black organic matter insoluble in alkalis is known as "humin"; a similar-looking insoluble product is obtained by the interaction of amino-acids and tryptophan, tyrosine and formaldehyde.[10]

Soil Acidity.—Much work continues to be done in America on

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[6] *Int. Mitt. Bodenk.*, 1920, **9**, 391.

[7] The multiplication of definite names for indefinite soil acids is confusing : it would be better to adopt the biological plan, and speak of ' A,' ' B,' ' C,' etc., terms which can easily be discarded when more precise definition is possible.

[8] H. Puchner, *Kolloid Zeitsch.*, 1919, **25**, 196 ; 1920, **26**, 159 ; *A.*, i, 274, 468.

[9] C. J. Schollenberger, *Soil Sci.*, 1920, **10**, 127.

[10] R. A. Gortner and G. E. Holm, *J. Amer. Chem. Soc.*, 1920, **42**, 632, 821 ; *A.*, i, 400, 450.

soil acidity. Four explanations have been offered of the power of soil to turn blue litmus red · selective adsorption (Cameron), the presence of organic acids (Sprengel), of acid silicates (Hopkins, Loew), of easily hydrolysable iron or aluminium salts which arise when supplies of basic calcium and magnesium compounds are low [11] (Abbott, Conner and Smaller, Daikuhara).

The existence of a definite hydrogen-ion concentration in acid soils shows the presence of definite acids, without, however, giving much information as to their nature.[12]

Aluminium nitrate and sulphate are both toxic to plants, especially clover, when applied in amounts equivalent to the acidity of the soil. Aluminium oxide and phosphate, on the other hand, had no effect.[13] It was further found that washing soil with a solution of potassium sulphate or nitrate removed its acidity, and also 59 per cent. of its aluminium. The leached soil was better suited for the growth of clover than the original acid soil. Addition of lime or calcium phosphate also overcame the acidity and made the soil fertile. These facts are all consistent with the view that aluminium is the toxic agent. It is further suggested that aluminium occurs as gibbsite, a form of aluminium oxide, readily soluble in acids, which during nitrification or "sulphofication." becomes converted into nitrate or sulphate. The weak point in the suggestion is that neither gibbsite nor other readily soluble aluminium oxide has commonly been found in soils in temperate climates, although it must be admitted that they have rarely been looked for.

An interesting test for sour soils is based on the fact that iron also, like aluminium, passes into solution when a potassium salt is added to a sour soil, but not when it is added to a normal neutral soil. Sourness therefore is readily detected by adding potassium thiocyanate, and still better by using an alcoholic solution of this substance.[14]

Soil acidity is now measured by: (1) the lime requirement or potassium nitrate extraction,[15] essentially titration methods indicat-

[11] See L. P. Howard, *Soil Sci.*, 1919, **8**, 313; *A.*, i, 416.

[12] For further evidence of the chemical origin of soil acidity, see H. A. Noyes, *J. Ind. Eng. Chem.*, 1919, **11**, 1040; *A.*, i, 211, and R E. Stephenson, *Soil Sci.*, 1919, **8**, 41; *A.*, i, 274. For details see E. T. Wherry, *J. Washington Acad. Sci.*, 1920, **10**, 217; *A.*, ii, 400.

[13] J. J. Mirasol, *Soil Sci.*, 1920, **10**, 153; *A.*, 1921, i, 88. '

[14] N. M. Comber, *J. Agric. Sci.*, 1920, **10**, 420.

[15] H. G. Knight, *J. Ind. Eng. Chem.*, 1920, **12**, 340; *A.*, i, 468. For a study of lime absorption by Indian soils and a method for ascertaining lime requirement, see F. J. Warth and M. P. Saw, *Mem. Dept. Agric. India*, 1919, **5**, 157; *A.*, i, 416.

ing the quantity of the acid; (2) the hydrogen-ion concentration (Sörensen's P_H notation is commonly used),[16] measuring the strength or intensity of the acid. On general grounds one would expect no necessary relationship between these quantities. As a matter of fact, it is now suggested[17] that they may be related, the observed inconsistencies arising from inaccuracies in the Veitch method commonly used in America, or from the presence of "buffers." Seeing, however, that "buffers" occur in all soils it would appear that exceptions would be frequent.

It has sometimes been asserted that the acidity of soil is too feeble to cause injury to plants, and the cause of the infertility must be sought elsewhere.

A set of measurements made in West Virginia[18] give the following optimum P_H values when phosphoric acid and sodium hydrate are the adjusting substances: seedlings of wheat, soja beans and lucerne, 5·94; seedlings of maize, 5·16. In more strongly acid solutions of soja beans and wheat suffered little until the value fell below 5·16; although lucerne suffered at once, 2·96 seems to be below the critical value, and 2·16 was fatal to growth (although not to germination) and favoured the growth of moulds in the cultures. Some injury was observed when the neutral point was attained and considerable injury when it was passed; alkalinity apparently is more harmful than acidity. Other measurements have been made with lucerne at New Jersey, sulphuric acid and calcium carbonate being here the adjusting substances. Germination was practically unaffected between P_H values 4·5 to 7·0; below 4·5, however, it was much retarded.[19] The yield showed a steady increase between P_H values 3·8 to 6·5, with some irregularities between 6·5 and 8. More measurements of this kind are needed; these results suggest slight acidity as the optimum condition, whereas long agricultural tradition favours neutrality attained by use of chalk or lime.

There is one case, however, where slight acidity is known to be desirable—the potato crop, which becomes liable to "scab" if the P_H value is too high. Gillespie gave 5·2 as the limiting value; a case is now known, however, where "scabbing" occurred at 4·8, although it was much reduced in comparison with the control plot at 5·6.[20] Acidification had been brought about by the addition of sulphur, which oxidises in the soil to form sulphuric acid. This method of controlling soil reaction promises to be of much interest.

[16] The student will find a full account of this method and a critical discussion by E. A. Fisher in *J. Agric. Sci.*, 1920, **11**, 19.

[17] A. W. Blair and A. L. Prince, *Soil Sci.*, 1920, **10**, 253.

[18] R. M. Salter and T. C. McIlvaine, *J. Agric. Res.*, 1920, **19**, 73.

[19] J. S. Joffe, *Soil Sci.*, 1920, **10**, 301.   [20] W. H. Martin, *ibid.*, 1920, **9**, 393.

Attempts have been made to ascertain in what way the acidity injures plants. The acidity of the sap corresponds with values 5·48 to 5·97 in buckwheat seedlings, and 4·82 in the adult plant;[21] there is also considerable reserve acidity.

These figures may be of the same order as those for optimum conditions in the soil. Some of the results lend colour to the suggestion[22] that the harmful effect of soil acidity exceeding these values is due to its influence in preventing plants from securing rapidly enough the bases necessary for neutralisation and precipitation of acids within the plant; in general, also, the addition of lime to the soil decreases the acidity of the plant juice.

The present position cannot be better described than in the words of D. R. Hoagland,[23] one of the foremost investigators of the modern aspects of soil problems:

"In perhaps the majority of cases the inhibition of crop growth frequently associated with acid soils may not be the direct effect of the acidity at all. In other factors, such as soluble aluminium, may be found the true direct cause of the injury. It is granted that these causes may be removed by exactly the same treatment which neutralises the acidity, but in the interest of scientific progress it is essential to separate and designate the various factors and their inter-relations.

"Is it not possible that the whole subject would become clarified if we attempted to reach such definite conclusions as: 'The growth of the crop is inhibited by too great concentration of hydrogen ion, or by too large a concentration of aluminium ion, or by too low a level of calcium in the soil solution, or by the effect of the hydrogen-ion concentration on the soil micro-organisms, etc.'?"

Methods of Increasing the Stock of Organic Matter in the Soil.

Considerable attention has been given to green manuring as a means of increasing the supplies of organic matter in the soil. Emphasis has again been laid on the value of leguminous crops, and some precise data have been accumulated.[24] Attempts (unfortunately not giving very definite results) have also been made to ascertain whether or not soil acidity is increased thereby.[25] Further evidence is published that in Virginia, as elsewhere, the growing crop temporarily restricts nitrification in soil, soja beans being an exception.[26]

[21] A. R. C. Haas, *Soil Sci.*, 1920, **9**, 341.
[22] E. Truog, *ibid.*, 1918, 5, 169. [23] *Private communication.*
[24] T. L. Lyon, J. A. Bizzell, and B. D. Wilson, *Soil Sci.*, 1920, **9**, 53.
[25] L. P. Howard, *ibid.*, 27. [26] R. C. Wright, *ibid.*, 1920, **10**, 259.

Soil Organisms.

The effectiveness of leguminous crops arises from the fact that they are associated with micro-organisms capable of fixing gaseous nitrogen and converting it into substances available for the nitrogenous nutrition of the plant. These remarkable organisms have been the subject of much investigation; a life-cycle has been suggested,[27] for which there is considerable evidence. Five stages are described: a small non-motile form, a larger non-motile coccus, an elliptical highly motile form (this being the swarmer stage of Beijerinck), a rod form, and finally, when the carbohydrate supply is exhausted, a vacuolated stage. A neutral reaction and the presence of calcium phosphate speed up the change from non-motile to motile forms. This work is being continued.

Some interesting work on the general biological relationships is being done in Professor A. L. Whiting's laboratory in Illinois. The process of nitrogen fixation was not adversely affected by nitrate or by organic matter; indeed, in the case of cow peas there was some evidence that the addition of organic matter increased it.[28]

Another important practical problem has been studied: whether the organisms are the same for all leguminous plants or whether there are special strains for each kind. Some degree of specificity is proved: the organism of lima bean (*Phaseolus limatus*) is identical with that of cow pea and will inoculate either crop, but it is distinct from that of navy and kidney beans (*Phaseolus vulgaris*), and will not inoculate these.[29]

Nitrates have a marked effect on nodule production. Soja beans take up these compounds readily from the soil; indeed, the concentration of nitrate in the cell sap becomes greater than in the soil solution, and so high as to inhibit growth and reproduction of the organism there.[30]

In addition to the fixation of nitrogen, bacteria play an important part in breaking down the protein contained in plant residues and producing nitrates needed for plant nutrition. Further data have been collected in New Jersey showing that the productiveness is closely related to the rate of evolution of carbon dioxide (described as " oxidising power "), and to a less extent to rate of nitrate accumulation and bacterial numbers.[31]

In a suggestive paper, which may foreshadow important develop-

[27] W. F. Bewley and H. B. Hutchinson, *J. Agric. Sci.*, 1920, **10**, 144.
[28] W. A. Albrecht, *Soil Sci.*, 1920, **9**, 275.
[29] A. L. Whiting and R. Hansen, *ibid.*, 1920, **10**, 291.
[30] W. H. Strowd, *ibid.*, 343.   [31] J. R. Neller, *ibid.*, 29.

ments, Gillespie draws a distinction between oxidations of high potential and those of low potential in a soil.[32] A given rate of absorption of oxygen or production of carbon dioxide may arise from an oxidation of high intensity or potential involving a small quantity of material, or a reaction of low potential involving much material. The phenomena are parallel to those of the hydrogen-ion concentration, and simultaneous development of both aspects of the subject may be expected.

Further work has been done on the protozoan fauna of the soil, and at last it appears that this subject is being put on a sound basis. The method of estimating the numbers of protozoa in natural soils has been greatly improved by D. W. Cutler at Rothamsted;[33] active forms can now be distinguished from cysts and separated out into a number of different species. The first systematic census [34] was taken at intervals of ten days, and the results when plotted, whilst definitely indicating certain relationships, showed many fluctuations which were difficult to understand. A daily count of the organisms in a field plot was therefore organised, and it revealed some remarkably interesting phenomena. The numbers of bacteria were always inversely proportional to the numbers of active amœbæ, whilst the numbers of flagellates showed a remarkable periodicity which is not yet explained. The results [35] are so important that the daily census is being continued for 365 consecutive days. American investigators have sometimes claimed that protozoa were absent or unimportant in American soils, which if true would indicate a great difference in micro-organic flora in this country and America. Using a less complete method of counting, it is now recognised that in the soil of New Jersey there is a fauna of organisms " which are practically always present in the soil in considerable numbers and which use the soil as a medium in which to live and carry on their life processes." The fauna, however, is believed to exist mainly in the non-trophic state.[36] It seems highly desirable that an extended quantitative survey should be made in at least as comprehensive a manner as is done at Rothamsted, discriminating carefully between active forms and cysts; there appears to be no simple direct method of doing this short of actual counts.

Advances in soil microbiology have shown that the soil population is more complex than was at one time thought, but it is also known that some degree of simplification often increases productive-

[32] L. J. Gillespie, *Soil Sci.*, 1920, **9**, 199.
[33] *J. Agric. Sci.*, 1920, **10**, 135.   [34] L. M. Crump, *ibid.*, 182.
[35] D. W. Cutler and L. M. Crump, *Annals of Applied Biol.*, 1920, **7**, 11.
[36] C. R. Fellers and F. E. Allison, *Soil Sci.*, 1920, **9**, 1.

ness. Simplification is obviously advantageous when disease organisms or pests are present. Some organisms tend normally to disappear in the general competition; the *Pseudomonas citri* causing citrus canker in America is rapidly exterminated from ordinary soil, although it flourishes in sterilised soil.[37] In other cases, however, competition alone is insufficient and direct control is attempted. Heat is found to be effective, but its application is rarely feasible. Recourse is therefore had to chemical methods, and substances are sought which, whilst toxic to the organism in question, will not injure the plant. This necessary limitation rules out most inorganic poisons, such as arsenic compounds, mercury salts, etc., and restricts investigators to organic substances. Applications to the soil of calcium sulphide and naphthalene or cymene lead to much increase in the crop and also in numbers of *B. butyricus*, although on fallow soils this particular anaerobic organism does not develop, but there is a loss of nitrogen.[38] In seeking for new . agents the first step is to ascertain the effect of various groupings on toxicity. In the case of the wireworm [39] aromatic compounds are more toxic than aliphatic compounds, and the toxicity is successfully increased by the addition of methyl (the least effective), halogen, hydroxyl, or methylamino-groups (most effective). Substitution in the side-chain is more effective than in the ring. The effect is not additive, however; position and other groups both exert great influence. The association of chlorine and nitro-groups is particularly potent, and chloropicrin is one of the most lethal agents tested. In series of compounds of the same chemical type there is a fairly close relationship between toxicity and vapour pressure, rate of evaporation and volatility, toxicity increasing as the volatility decreases, until finally, a limit is reached when the vapour pressure sinks too low to allow of the attainment of a toxic concentration.

Somewhat similar, although less extensive data, are recorded with *Paramoecium*.[40]

A substance highly toxic to the organism, however, will not necessarily suppress it in the soil, as the soil population includes organisms able to effect remarkable decompositions, for example, to break down such unlikely substances as phenol, cresol, and apparently even naphthalene and more stable ring compounds. Owing

[37] H. A. Lee, *J. Agric. Sci.*, 1920, **19**, 189; H. R. Fulton, *ibid.*, 207.

[38] G. Truffaut and N. Bezssonoff, *Compt. rend.*, 1920, **171**, 268; *A.*, i, 655.

[39] F. Tattersfield and A. W. R. Roberts, *J. Agric. Sci.*, 1920, **10**, 199. Among possible agents, trichloroethylene deserves consideration: E. Salkowski, *Biochem. Zeitsch.*, 1920, **107**, 191; *A.*, i., 794, shows that it is cheap, volatile, and effective.

[40] N. McCleland and R. A. Peters, *J. Physiol.*, 1919, **53**, xii, xv; *A.*, i, 512.

to the smallness of the amounts involved and the complex nature of soil, it is difficult to ascertain the course of the decomposition, but some help may be obtained from the work of chemists on the catalytic oxidation of simple but stable organic compounds.[41]

The case of vanillin has been studied in some detail.[42] This substance has been isolated from soil,[43] and it is toxic to plants; it is, however, decomposed by certain soil bacteria. Apparently only a limited number of organisms have this power. It is obvious that micro-organisms capable of breaking down potential plant toxins are of importance in soil fertility.

A further unexpected change apparently brought about by bacteria is the oxidation of the element sulphur when added to the soil. This was first demonstrated in 1916,[44] and was turned to practical account in the conversion of mineral phosphates into soluble phosphate in compost heaps or in the soil. Further details are now worked out, and it is shown that nitrification still proceeds in spite of the formation of acid.[45]

An interesting observation has been made in Egypt to the effect that the fallow or "sheraqi" is a period of biological inactivity in the soil, but is followed by a period of increased activity, the phenomena being apparently parallel to those shown during partial sterilisation of the soil.[46]

In some cases, probably in many, a reaction is brought about by a chain of agencies, chemical and biological. Thus, calcium cyanamide is a well-known fertiliser, but it owes its effectiveness to the ammonia produced in its decomposition. The first stage is the production of carbamide; this is apparently non-biological, since it occurs even after the soil is heated to 135°; the decomposing agent is not yet identified, although the change can be brought about by certain zeolites which may occur in soil. The second stage is the formation of ammonia from the carbamide; this is biological and can be effected by numerous micro-organisms.[47]

An improved method of determining ammonia in soil has been developed.[48]

[41] For example, paraffins: A. Grün, *Ber.*, 1920, **53**, [B], 987; *A.*, i, 518; benzene: J. M. Weiss and C. R. Downs, *J. Ind. Eng. Chem.*, 1920, **12**, 228; *A.*, i, 426.

[42] W. J. Robbins and E. C. Lathrop, *Soil Sci.*, 1919, **7**, 475; *A.*, i, 265; W. J. Robbins and A. B. Massey, *ibid.*, 1920, **10**, 237; *A.*, i, 913.

[43] E. C. Shorey, *J. Agric. Res.*, 1914, **1**, 357; *A.*, 1914, i, 946.

[44] J. G. Lipman, H. C. McLean, and H. C. Lint, *Soil Sci.*, 1916, **2**, 499. For bibliography, see H. C. McLean, *ibid.*, 1918, **5**, 251.

[45] O. M. Shedd, *J. Agric. Res.*, 1919, **18**, 329.

[46] J. A. Prescott, *J. Agric. Sci.*, 1920, **10**, 177.

[47] G. A. Cowie, *ibid.*, 163; *A.*, i, 655.   [48] D. J. Matthews, *ibid.*, 72.

The effect of water supply on bacterial activity has been studied and some useful curves have been drawn; relationships have also been traced with some of the Brigg's and Hilgard's constants.[49]

Relation of Soils to Plant Growth: Water Supply.

One of the most important functions of the soil is to supply water to the plant. This problem has been extensively studied by Livingstone, and he now contributes an important suggestion that may help materially in elucidating the very complex phenomena concerned.[50] The fundamental conception is to regard the soil as a machine delivering water to the absorbing surface of the plant roots; the purpose of the investigation is to study the water-supplying power of the soil. The problem is regarded dynamically, although, of course, it depends on a number of static conditions, such as sizes, kinds, and arrangement of the soil particles, and the water content per unit volume. The experimental method consists in embedding porous porcelain cones in the soil, then after a suitable time withdrawing them and weighing to measure the absorbed water. Special attention is paid to the region of moisture contents where wilting occurs. It appeared from the data obtained (although the authors frankly recognise their preliminary nature) that the water-supplying power at the wilting point was approximately the same for all the twelve soils examined. This critical value is, of course, not to be regarded as a constant for all kinds of plants and all degrees of evaporation, any more than is the wilting coefficient of Briggs and Shantz, which varies in a regular and predictable way for any given soil and plant with the evaporating power of the air.[51] If further investigation confirms the view that the value is independent of the physical make-up of the soil and is the same for sand, loam and humus, it will undoubtedly prove of importance.

The power to supply water, however, is dependent on the amount present, and this is the balance of gains over losses. The loss of water from the soil takes place partly by drainage and partly by evaporation. It is claimed that the rate of evaporation is diminished on addition of soluble salts, and the diminution is directly related to the osmotic concentration of the soil solution.[52]

The water relationships for soils are very complex, and a valuable critical résumé of the whole subject has been made by Keen.[53]

[49] J. E. Greaves and E. G. Carter, *Soil Sci.*, 1920, **10**, 361.

[50] B. E. Livingstone and R. Koketsu, *ibid.*, 1920, **9**, 469.

[51] J. S. Caldwell: The relation of environmental conditions to the phenomenon of permanent wilting in plants, *Physiol. Res.*, 1913, **1**, 1.

[52] M. I. Wolkoff, *Soil Sci.*, 1920, **9**, 409; *A.*, i, 803.

[53] B. A. Keen, *J. Agric. Sci.*, 1920, **10**, 44.

An attempt has also been made to analyse more closely the capillary movement of water through soil.[54]

An important factor, determining not only water supply, but tilth, ease of working the soil, and other properties, is the degree of flocculation of the finer particles. In practice, lime is used to effect this change, but the phenomena do not altogether fall in line with those ordinarily observed with colloids. Some of the apparent contradictions are elucidated in a very suggestive paper by Comber. " Silt," the fine but not the finest material in the soil, is most easily flocculated by calcium salts when the suspension is neutral; this is the usual behaviour of insoluble substances. On the other hand, " clay," the finest material, is most easily flocculated in alkaline suspensions. This is unusual for insoluble substances, but is shown by silicic acid and some of the so-called " emulsoid " colloids. It is suggested that clay as an emulsoid protects the larger particles, which by themselves are suspensoid, and causes the whole soil to be flocculated by lime. In absence of clay, however, lime does not effect flocculation.[55]

Alkali Soils.

Under conditions of low rainfall, salts of sodium may accumulate in soils and produce sodium carbonate by various interactions, which are not yet fully understood.[56] It is suggested that the sulphate may in some cases be reduced to sulphide, which is then decomposed by carbon dioxide to form the carbonate.[57]

However they are formed in the soil, the harmful effects of sodium carbonate, sodium chloride, and other salts on plants and on organisms causing ammonification and nitrification are overcome by the addition of calcium sulphate. In the case of microorganisms, ferric chloride and sulphate are also effective.[58]

Doubt is now thrown on the current values for the toxicity of these salts in soils. It is shown that soil absorbs more water from a solution of sodium carbonate than from an equivalent solution of sodium chloride, and therefore, under conditions apparently comparable, the plant root would be in contact with a more concentrated solution of carbonate than of the chloride. This fact is said to have been overlooked, and to have

[54] W. Gardner, *Soil Sci.*, 1920, **10**, 103, 357.
[55] N. M. Comber, *J. Agric. Sci.*, 1920, **10**, 425. For other experiments, see O. M. Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 460; *A.*, ii, 296.
[56] For a recent discussion, see A. de Dominicis, *Staz. sper. agr. Ital.*, 1918, **51**, 103; *A.*, i, 414.
[57] E. Pozzi-Escot, *Bull. Soc. chim.*, 1919, [iv], **25**, 614; *A.*, ii, 185.
[58] J. E. Greaves, *Soil Sci.*, 1920, **10**, 77.

led to false conclusions as to the relative toxicity of these substances.[59]

Other Investigations.

Further experiments are reported showing that calcium sulphate increases the amount of soluble matter in soils.[60] The amount of water-soluble material in the soil is not greatly affected by normal variations from the mean moisture content, but it is reduced when air-dry or water-logged conditions are attained.[61]

Work on the drift soil of the Craibstone Farm has been continued.[62] This soil is largely composed of disintegrated granite. Like other soils, it has a marked power of absorbing ammonia, and the property is not shown by all-constituents alike, but chiefly by the finer fractions. Powdered granite shows similar powers of absorption. It is not necessary to assume, therefore, that absorption is effected only by decomposed material. Absorption is decreased after ignition.

Fertilisers.

Following the practice of the previous years, the technical aspects of this part of the subject will be discussed in the Report to the Society of Chemical Industry, and only a few of the papers of scientific interest will be referred to here.

Two summaries of long-continued field experiments have been issued. In the New Jersey experiments, the best results were given by sodium nitrate on the unlimed, and ammonium sulphate on the limed, plots, whilst the organic manures (dried fish, dried blood, and tankage) were less effective. No more than one-third of the added nitrogen was recovered in the crop, and, in absence of leguminous plants, there was no accumulation of nitrogen in the soil, but, on the contrary, a loss.[63] In the Ohio experiments summarised by Director Thorne, very similar results were obtained; sodium nitrate proved better than ammonium sulphate on unlimed, but not on limed, soils, and both proved better than tankage.[64] One case is reported, however, where an organic manure proved more effective than others, namely, that of the American "blueberry." Sodium nitrate by itself somewhat depressed the yield;

[59] T. H. Kearney, *Soil Sci.*, 1920, **9**, 267 ; *A.*, i, 588.
[60] M. M. McCool and C. E. Millar, *J. Agric. Res.*, 1920, **19**, 47 ; *A.*, i, 588.
[61] J. C. Martin and A. W. Christie, *ibid.*, 1919, **18**, 139.
[62] W. G. Ogg and J. Hendrick, *ibid.*, 1920, **10**, 333, 343.
[63] J. G. Lipman and A. W. Blair, *Soil Sci.*, 1920, **9**, 371.
[64] C. E. Thorne, *ibid.*, 487.

complete artificial manure somewhat increased it, but a mixture of the latter and dried blood considerably increased it. The manuring of fruit has, however, always been a subject of some difficulty, bristling with exceptions to all the rules.[65]

In all fertiliser work, it is necessary to carry out field trials, and, in spite of their apparent simplicity, they are liable to many sources of error. A useful summary has been prepared of the methods by which the more serious errors can be avoided, special stress being laid on Larsen's method.[66]

The effect of magnesium carbonate on plant growth is a subject of much practical importance; a persistent idea is current among practical men that it is in some way harmful to crops, and, in consequence, magnesium limestone is not held in high repute. Many experiments have been made. Recently, in Indiana, magnesite proved more favourable than calcite for nitrification and for multiplication of aerobic and anaerobic bacteria on a yellow clay soil, but not on a black soil; it produced a greater increase in soluble salts in the soil, and led to larger increases in yield of beet, but smaller increases of wheat and clover, than did calcite.[67] On the other hand, it is claimed that full crops are not obtainable on soils where magnesia is in excess of lime.[68]

Plant Growth.

The nutrient salts absorbed by plants from soil, together with the carbon dioxide assimilated by their leaves, are elaborated into the complex constituents and contents of the plant cells. The processes involved continue to form the subject of much investigation. The relationships between absorption of salts by the plant root and composition of the nutrient medium is being studied at the California Experimental Station, where, in the case of barley, three distinct phases in the absorption of the nutrients were found.[69] Up to the time of formation of the head, the rate of absorption progressively increases until, finally, the amounts of nitrogen and of potassium reach a maximum. The second phase corresponds with the translocation of material into the developing heads; this is marked, not only by a decreased rate of absorption from the soil, but by definite and substantial losses of nitrogen, potassium, and apparently calcium from the aerial parts of the

[65] C. S. Beckwith, *Soil Sci.*, 1920, **10**, 309.

[66] J. Sebelien, *J. Agric. Sci.*, 1920, **10**, 415.

[67] S. D. Corner and H. A. Noyes, *J. Agric. Res.*, 1919, **18**, 119.

[68] J. Hughes, *J. Bath and W. and S. Co. Soc.*, 1919, [v], **13**; *A.*, i, 416.

[69] J. S. Burd, *J. Agric. Res.*, 1919, **18**, 61.

plant, and presumably from the whole plant, although difficulties of manipulation make root examination uncertain. Towards the end of the period, the lost materials are regained. The final stage is ripening, during which absorption ceases and losses are resumed. It is suggested that these movements of salts into and out from the plant may be due to purely physical causes, as low concentration of the water extract of the soil occurs simultaneously with the movement out from the plant. The results suggest that the normal relationship between plant and soil is to have a relatively high soil concentration in the early stages of growth and a low concentration in later stages.

Reference has been made in earlier Reports to the work of Shive and Tottingham, in which it is claimed that plants need not only an adequate supply of various nutrient substances, but also some kind of relationship or "physiological balance" between the particular elements. The data show considerable variations, but the ratio of nutrients causing maximum growth is called the optimum ratio. This ratio is found to alter with the concentration of the nutrient solution; it is not the same at 0·1, 1·75, and 4 atmospheres,[70] but it is unaffected by the nature of the medium, being the same in sand as in water culture. So also it is independent of variations in the moisture content of the sand, and is the same for degrees of moistness varying from 40, 60, to 80 per cent. of the water-retaining capacity of the sand. It is not, however, constant for the whole range of growth of the plant, being different in seedling and adult stages, and different for the growth of "top" and of the roots.

Closely associated with this conception of physiological balance is that of antagonistic action between ions. Wheat seedlings are adversely affected by sodium chloride and sodium sulphate, but the toxic effects are largely overcome by small amounts of calcium oxide or calcium sulphate, and to a less extent by magnesium sulphate and barium chloride. The lime did not prevent the entrance of the sodium salts into the plant; its antagonistic effect was therefore not attributable to any reduction of permeability.[71]

Calcium salts also enable the plant to overcome the harmful effects of copper salts, although they do not prevent the entry of copper into the plant. It is considered more probable that the calcium favours the evolution of the plant, giving it greater vigour, and in particular greater volume, into which the copper diffuses, thus preventing dangerous accumulation in any one region.[72]

[70] J. W. Shive, *J. Agric. Res.*, 1920, **18**, 357.

[71] J. A. LeClerc and J. F. Breazeale, *ibid.*, 347; *A.*, i, 413.

[72] L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, **170**, 420; *A.*, i, 357.

Attention has, however, been directed to the possibility that certain ions may alter the plasma colloids[73] or the permeability of the plant cells.[74] Ferrous salts are known to be more injurious to young plants than ferric salts, and therefore any condition which favours their oxidation reduces the toxic effects. It is shown that monopotassium phosphate and copper sulphate both have this effect.[75] Neither manganese sulphate nor chromium salts were found effective as fertilisers.[76]

The functions of the various nutritive elements are determined indirectly. Some work has been done this year on calcium.[77] There seems to be a close relationship between the calcium and nitrogen content of plants, and the more important crops can be divided into two groups: (a) those with low content of calcium and nitrogen, a low calcium–nitrogen ratio, and low lime require-ments; (b) those with high content of calcium and nitrogen, high ratio, and high lime requirement. It is suggested that protein metabolism is probably one of the chief sources of plant acids, and may give rise to the need for calcium.

The question whether silicon is necessary for plant nutrition has been raised. An artificial calcium silicate was tested against calcium carbonate, and found to be in no way superior. It appears, therefore, that silicon in this compound is of no advantage to the growing crop.[78]

An interesting and entirely novel suggestion as to the function of potassium in plants has been brought forward. It is claimed[79] that the potassium ion may, as regards function, be replaced by all the other radioactive elements, heavy or light, provided the doses are equiradioactive; it may also be replaced by a free radio-active radiation.

Some attention has been given to the action of copper salts on vegetation. It is shown that copper is a frequent, and possibly a normal, constituent of plants.[80] It is claimed, in spite of

[73] T. Tadokoro, *J. Coll. Agr. Hokkaido. Imp. Univ.,* *Sapporo, Japan,* 1919, **8,** 143; *A.,* i, 585; S. M. Neuschlosz, *Pflüger's Archiv,* 1920, **181,** 17; *A.,* i, 698.

[74] O. L. Raber, *J. gen. Physiol.,* 1920, **2,** 535, 541; *A.,* i, 585, 586.

[75] L. Maquenne and E. Demoussy, *Compt. rend ,* 1920, **171,** 218; *A.,* i, 654.

[76] T. Pfeiffer, W. Simmermacher, and A. Rippel, *Fühlings Landw. Zeit.,* 1918, 313; *A.,* i, 652; F. Weis, *K. Vet.-Landbohöjskole Aarsskrift,* 1919, 239; *A.,* i, 652.

[77] F. W. Parker and E. Truog, *Soil Sci.,* 1920, **10,** 49; *A.,* i, 702.

[78] B. L. Hartwell and F. R. Pember, *ibid.,* 57.

[79] H. Zwaardemaker, *J. Physiol.,* 1920, **53,** 273; *A.,* i, 511; *Pflüger's Archiv,* 1918, **173,** 28; *A.,* i, 345.

[80] E. Fleurent and L. Lévi, *Bull. Soc. chim.,* 1920, [iv], **27,** 440, 441; *A.,* i, 584.

previous work to the contrary, that dilute solutions of copper sulphate added to water cultures have a favourable action on the growth of roots and stems of peas and wheat.[81]

Theoretical discussions have been attempted[82] of the physico-chemical basis of the phenomena of absorption and elaboration of nutrient salts, and of the effects of these salts on cell division.[83]

For many years it was supposed that nitrates, phosphates, and simple salts of potassium, calcium, magnesium, etc., were alone necessary to plant growth, no organic compound of any kind being required. Recently it has been asserted that certain organic compounds are helpful, if not necessary, and lead to marked increases in growth. The case of *Lemna major* has been studied in London; crude nucleic acid derivatives from bacterised peat, the growth products from *Azotobacter chrococcum* and *Bacillus radicicola*, leaf mould, fresh and well-rotted stable manure, and well-manured fertile soil all contained water-soluble substances which promoted the growth of this organism.[84] In California, dilute extracts of peat (10 parts in 1,000,000 of water) produced a marked stimulation of root growth of citrus seedlings,[85] which could not be obtained with corresponding solutions of sodium nitrate or potassium chloride. On the other hand, bouillon prepared from fresh brewers' yeast, which had been heated to 135° and rendered incapable of curing polyneuritis in pigeons, was still effective in improving the growth of fungi.[86]

Assimilation.—The ease and rapidity with which the plant in sunlight absorbs carbon dioxide and converts it into sugar has always been a source of wonder to chemists, who have never yet been able to reconstruct the process.

Support is periodically forthcoming for Baeyer's old hypothesis; it is claimed[87] that formaldehyde can be absorbed by plant leaves and transformed into plant tissue. There are, however, difficulties in the way of this hypothesis, and another has been put forward, which is claimed to be more in accordance with the facts. The first stage is supposed to be the isomerisation of carbon dioxide, with the formation of a secondary peroxide, $>C<^{O\cdot OH}_{OH}$; this

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[81] L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, **170**, 1542; *A.*, i, 584.

[82] E. Reinau, *Zeitsch. Elektrochem.*, 1920, **26**, 329; *A.*, i, 799.

[83] J. Spek, *Koll. Chem. Beihefte*, 1920, **12**, 1; *A.*, i, 353.

[84] W. B. Bottomley, *Proc. Roy. Soc.*, 1920, [B], **91**, 83; *A.*, i, 265; F. A. Mockeridge, *Biochem. J.*, 1920, **14**, 432; *A.*, i, 704.

[85] J. F. Breazeale, *J. Agric. Res.*, 1919, **18**, 267.

[86] A. Lumière, *Compt. rend.*, 1920, **171**, 271; *A.*, i, 652.

[87] M. Jacoby, *Biochem. Zeitsch.*, 1919, **101**, 1; *A.*, i, 800.

eliminates oxygen and yields the group $>C<^H_{OH}$, which is predisposed towards condensation. Chlorophyll is assumed to sensitise the preliminary isomerisation and to act as catalyst in the final condensation.[88]

Another hypothesis [89] is that the carbon dioxide polymerises to form tetrahydroxyethylene, and this passes over into the keto-form:

$$O=C=O \atop O=C=O \quad +2H_2 \Big| O \rightarrow \quad {HO-C-OH \atop HO-C-OH} \rightarrow \quad \begin{matrix} H \\ O-C-OH \\ \diagdown \\ HO-C-O \\ H \end{matrix} \Big| +O_2$$
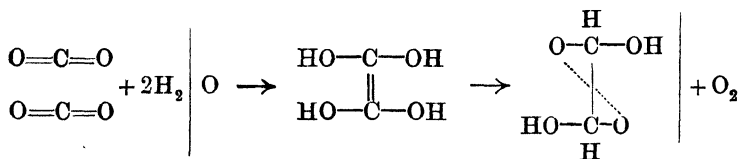
which contains the characteristic sugar grouping $\begin{matrix} H \\ HO-C-O \\ | \quad | \end{matrix}$.

The formation of plant acids, sugars, etc., is easily deduced.

Some of the physical phenomena associated with the process have been investigated; the effect of various factors on its velocity,[90] and the fact that colloidal chlorophyll is much more sensitive to light than the natural product, although the sensitiveness can be depressed by various agents [91]; and the fluorescent phenomena studied by the spectroscope.[92]

The process has also been discussed from the point of view of its dependence on the internal pressure of carbon dioxide in plants.[93] A simpler form of apparatus for the study of photosynthesis has been described.[94]

From time to time it has been suggested that the growth of plants ought to be increased by additions of carbon dioxide to the atmosphere, and some instances of increase so obtained in a glasshouse are given.[95] Field applications of this method may not be feasible, but under glass there may be possibilities worth investigating.

It is usually supposed that nitrogen is necessarily assimilated in the form of some simple compound, such as nitrate, ammonia, or

[88] G. Woker, *Pflüger's Archiv*, 1919, **176**, 11; *A.*, i, 354.

[89] P. R. Kögel, *Zeitsch. wiss. Photochem.*, 1920, **19**, 215; *A.*, i, 355.

[90] O. Warburg, *Biochem. Zeitsch.*, 1919, **100**, 230; 1920, **103**, 188; *A.*, i, 583, 798.

[91] R. Wurmser, *Compt. rend. Soc. Biol.*, 1920, **83**, 437; *A.*, i, 560.

[92] K. Stern, *Ber. Deut. bot. Ges.*, 1920, **38**, 28; *A.*, i, 700.

[93] E. Reinau, *Chem. Zeit.*, 1919, **43**, 339; *A.*, i, 128.

[94] W. J. V. Osterhout, *Bot. Gaz.*, 1918, **68**, 60; *A.*, i, 128.

[95] M. B. Cummings and C. H. Jones, *Bull.*, 1919, **211**, 56 pp.; *A.*, i, 267. See also F. Riedel, *Stahl und Eisen*, 1919, **39**, 1497.

carbamide,[96] and it is certainly true that assimilation usually proceeds in this way. Periodically, it has been assumed that gaseous nitrogen might be assimilated by higher plants, but the possibility has not been taken seriously by physiologists. It is known, however, that certain bacteria can effect this assimilation, and from gaseous nitrogen and carbohydrates can synthesise cell proteins; but these bacteria have no power of synthesising carbohydrates: they are dependent on pre-formed sources of these materials. Moore has made the interesting announcement that certain unicellular algæ possess the power of fixing, not only gaseous nitrogen, but carbon also, so that they can by themselves, and without pre-formed carbohydrates, construct the whole organic contents of their cells.[97] If this result is confirmed, it will alter some of the fundamental conceptions of soil microbiology and plant physiology.

The Growth of Plants: Effect of Light and Temperature.—Investigators dealing with the growing plant are soon compelled to realise the dominating effect of factors other than the supply of plant nutrients. One of the most important is light. The rate of growth is directly proportional to the length of the day, and this factor also profoundly affects the sexual reproduction of plants; in many species the flowering and fruiting stages can be attained only when the length of day falls within certain limits, for example, in natural conditions only during certain seasons.[98] In absence of sufficient day length, vegetative growth may continue more or less indefinitely, thus leading to the phenomena of gigantism; or, on the other hand, under the influence of suitable day length, precocious flowering and fruiting may be induced. In some cases, a day length was found suitable both to vegetative growth and reproduction; an ever-blooming or ever-bearing habit was then obtained. By suitable variation of the length of day, it was possible to give annuals a perennial habit, or, on the other hand, to hasten their processes, so that they would go through two cycles of alternate vegetative and reproductive activity in one season. Variations in intensity of light had little effect, the normal intensity, as shown by H. T. Brown, being more than sufficient for the needs of the plant.

Moisture supply and temperature are equally important factors: these have been invoked to explain the stunted growth in wind-

[96] T. Bokorny, *Pflüger's Archiv*, 1918, **172**, 466; *A.*, i, 413, shows that carbamide is utilisable in proper conditions.

[97] B. Moore and T. A. Webster, *Proc. Roy. Soc.*, 1920, [B], **91**, 201; *A.*, i, 466.

[98] W. W. Garner and H. A. Allard, *J. Agric. Res.*, 1920, **18**, 553.

swept districts, evaporation being so marked that the plant is seriously cooled and deprived of adequate water supply. When these factors are made good, wind does little harm to crop growth.[99]

Of the numerous specialised papers, two may be mentioned. It is shown that cereal seeds can withstand dry heat to a temperature of 100° for some hours without serious loss of germinating power, whilst some of the disease spores affecting seeds were killed.[1]

Studies have been made on somewhat similar lines of wilt-producing fungi, temperature having been found which will keep them in check without unduly damaging the plant.[2]

Composition of Crops.

Few problems present greater difficulty than those associated with the composition of crops. Farmers grow crops in order to sell them, but neither they nor the purchasers know what is in them. Little is known of the composition of crops, and, unfortunately, it is proving very difficult to arouse any interest in this or the closely allied subject of quality in crops.

The oat crop is one of the most important to the farmer, and it has been studied in detail by Berry at the West of Scotland Agricultural College.[3] A mass of analytical data is presented which is by far the most extensive hitherto available in this country. Various relationships were found between weight and composition of the kernel; with the thin, husked, white grains, as the kernel increased in weight the proportion of husk decreased, the oil and fibre diminished, whilst the carbohydrates, the yield of grain, and the proportion of grain to total produce increased. It is an important practical observation that the yield per acre is associated directly with the average size of individual grains, whilst the production of straw varies in the opposite direction.

The composition of the grain was affected by variation in organic matter content of the soil, for example, ploughed-up grassland and arable land, but season produced comparatively little effect, and artificial fertilisers still less. Locality, however, had a marked effect.

Investigations on the wheat crop on somewhat similar lines have been made at the University of Manitoba.[4] In an important paper it is shown that the protein content of wheat is much affected by climatic factors, by restriction of water supply, and by varietal

[99] L. Hill, *Proc. Roy. Soc.*, 1921, [B], **92,** 28.

[1] D. Atanasoff and A. G. Johnson, *J. Agric. Res.*, 1920, **19,** 379.

[2] H. A. Edson and M. Shapovalov, *ibid.*, 1**8,** 511.

[3] R. A. Berry, *J. Agric. Sci.*, 1920, **10,** 359.

[4] H. E. Roberts, *J. Agric. Res.*, 1920, **10,** 121.

factors. In breeding new varieties for general purposes, it is suggested that strains should be sought which vary greatly in their protein content, since a wide starch–protein ratio would probably mean greater climatic adaptability. For restricted areas, however, wheats of maximum protein content should be sought. The reduction of protein subsequent on irrigation can be largely counterbalanced by introducing lucerne into the rotation.[5]

Plant Constituents.

Constant additions are being made to the long list of plant constituents, and little more than the briefest reference is possible here. Until the function of a substance is known, the mere fact of its presence is not necessarily of much physiological interest.

Cellulose, Lignin, etc.—These substances constitute the larger portion of the material of the plant structure, and steady progress is being made with the knowledge of their constitution.[6] Perhaps the most important paper on this subject is a critical discussion of the constitution of cellulose.[7] Lignin has also been the subject of investigation; it has received the formula $C_{40}H_{40}O_{11}$, and is supposed to be built up from pentoses.[8]

Plant Pigments.—*Flavones* are yellow pigments; those obtainable from the tulip[9] and from Rhus[10] have been studied.

Anthocyanins are formed from flavones by reduction. The red pigment of the young leaves of the grape vine is regarded as identical with œnidin, the anthocyanidin derived from the pigment of the purple grape. This is the first instance recorded in which the red leaf pigment is an anthocyanidin.[11]

Members of the beet-red group of anthocyanins have been found in the skins of fuchsia and cacti berries, and in the petals of scarlet cactus flowers.[12]

Anthocyanins are further reducible to leuco-bases.

The tinctorial properties of a number of the anthocyanins have been studied.[13]

[5] J. S. Jones, C. S. Cohen, and H. P. Fishburn, *J. Agric. Sci.*, 1920, **10**, 290.

[6] P. Klason, *Arkiv Kem. Min. Geol.*, 1917, **6**, No. 15; *A.*, i, 148.

[7] K. Hess and W. Wittelsbach, *Zeitsch. Elektrochem.*, 1920, **26**, 232; *A.*, i, 532.

[8] P. Klason, *Arkiv Kem. Min. Geol.*, 1917, **6**, No. 15; *A.*, i, 148.

[9] B. Harrow and W. J. Gies, *Proc. Soc. Expt. Biol. Med.*, 1918, **16**, 8; *A.*, i, 70.

[10] C. E. Sando and H. H. Bartlett, *Amer. J. Bot.*, 1918, **5**, 112; *A.*, i, 272.

[11] O. Rosenheim, *Biochem. J.*, 1920, **14**, 178; *A.*, i, 467.

[12] F. Kryz, *Oesterr. Chem. Zeit.*, 1920, **23**, 55; *A.*, i, 515.

[13] A. E. Everest and A. J. Hall, *J. Soc. Dyers and Col.*, 1919, **35**, 275; *A.*, i, 70.

Sugars and Other Carbohydrates.—An improved method for detecting dextrose in plants has been described.[14] Both gentianose and sucrose have been detected in the roots of *Gentiana cruciata* and *G. purpurea.*[15]

Primeverose has been isolated from *Primula officinalis;* it is a biose formed by combination of a molecule of dextrose and a molecule of xylose, and it has a free aldehyde group.[16]

Inulin is the storage product in some plants, notably the artichoke. It does not occur in the leaves, but is formed in the stem and the tuber, presumably from the dextrorotatory carbohydrates supplied to the leaves.[17]

Odorous Constituents.—The odorous constituents of apples have been found to consist essentially of the amyl esters of formic, acetic, and hexoic acids, with a very small amount of the octoic ester, and, in addition, acetaldehyde, and probably some free acid.[18]

Proteins.—Osborne has continued his work on plant proteins, and has turned to the difficult problem of the leaf proteins, spinach being selected for examination. At least 40 per cent. of the total nitrogen of the leaves was found in the form of colloidal protein, which, however, may be in some form of combination with a substance of pentosan nature. A nearly colourless protein was, however, obtained.[19]

Two globulins and an albumin have been extracted from the Georgia velvet bean.[20] Globulins have been extracted from the coconut (*Cocos nucifera*)[21] and the jackbean (*Canavalia ensiformis*),[22] whilst phaseolin has been studied,[23] and also the proteins of polished rice.[24]

Alkaloids.—Nicotine is not present in the seed of tobacco; it is, indeed, harmful to germination, but it appears in the young plant immediately the chlorophyll begins to function, and it originates in the leaves. In case of injury, for example, cutting, the alkaloid is produced in increased quantity in the adjoining tissues. It is

[14] E. Bourquelot and M. Bridel, *Compt. rend.*, 1920, **170**, 631 ; *A.*, ii, 337.

[15] M. Bridel, *J. Pharm. Chim.*, 1920, [vii], **21**, 306 ; *A.*, i, 467.

[16] A. Goris and C. Vischniac, *Compt. rend.*, 1919, **169**, 871, 975 ; *A.*, i, 14.

[17] H. Colin, *Bull. Assoc. Chim. Sucr.*, 1919, **37**, 121 ; *A.*, i, 358.

[18] F. B. Power and V. K. Chesnut, *J. Amer. Chem. Soc.*, 1920, **42**, 1509 ; *A.*, i, 653.

[19] T. B. Osborne and A. J. Wakeman, *J. Biol. Chem.*, 1920, **42**, 1 ; *A.*, i, 516.

[20] C. O. Johns and H. C. Waterman, *ibid.*, 59 ; *A.*, i, 515.

[21] C. O. Johns, A. J. Finks, and C. E. F. Gersdorf, *ibid.*, 1919, **37**, 149; *A.*, i, 210.   [22] J. B. Sumner, *ibid.*, 137 ; *A.*, i, 210.

[23] A. J. Finks and C. O. Johns, *ibid.*, 1920, **41**, 375 ; *A.*, i, 401.

[24] J. Kurosawa, *J. Tokyo Chem. Soc.*, 1919, **40**, 551 ; *A.*, i, 414.

supposed, therefore, that nicotine is elaborated by the plant from certain residues of the nitrogen katabolism, either to prevent accumulation of these residues or to utilise them with intensification of their harmfulness in defence of its organs.[25]

Lycorine, $C_{16}H_{17}O_4N$, has been found in various plants of the order Amaryllidaceæ.[26]

Hydrogen Cyanide.—Considerable technical importance attaches to the occurrence of hydrogen cyanide in plants. This substance usually occurs in glucosidal combination, as in bitter almonds, cherry laurel leaves, seeds of *Phaseolus lunatus*, etc. It may also occur, however, in non-glucosidal form, in the buds of the cherry laurel and the young leaves of *Sambucus niger*.[27]

Enzymes.—It is not proposed to discuss here the general problem of enzyme activity, but reference must be made to one paper. The peroxydasic function in plants, which appears to be shown by living cells only,[28] and is usually attributed to enzymes, now appears to be due to iron compounds, katabolic products of more complex compounds, such as næmatoids, which, in virtue of their physical state, are able to act between the oxidisable substances and the peroxides.[29]   E. J. RUSSELL.

[25] L. Bernadini, *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 62 ; *A.*, i, 412.

[26] K. Gorter, *Bull. Jard. bot. Buitenzorg*, 1920, [iii], **1**, 352 ; *A.*, i, 467.

[27] L. Rosenthaler, *Schweiz. Apoth. Zeit.*, 1919, **57**, 571 ; *A.*, i, 271.

[28] J. G. McHargue, *J. Amer. Chem. Soc.*, 1920, **42**, 612 ; *A.*, i, 406.

[29] G. Gola, *Atti R. Accad. Lincei*, 1919, [v], **28**, ii, 146 ; *A.*, i, 208.

CRYSTALLOGRAPHY AND MINERALOGY.

THE striking renewal of activity in the subjects under review in this Report is all the more gratifying because they were among the first to suffer from the outbreak of war. The volume of work to be noted is, indeed, so considerable that space will not allow some investigations to be treated in accordance with their intrinsic merits. This is especially the case perhaps in the province of crystal-structure. In the first place, there are to be noted two books of more than ordinary value. The one by Niggli [1] not only contains a full and clear account of all the point-systems, but also brings the subject up to date in the light of X-ray methods and results. Sommerfeld's book [2] is more general, covering, in fact, recent developments in a wide field of physical discovery and interpretation, to which the study of crystals has contributed so powerfully. Then there are two important contributions to the related subjects of atomic distances and volumes, and also many successful reconstructions of crystals, all of which will receive due notice. On the other hand, an ingenious development of X-ray technique [3] must be disposed of here somewhat summarily. The method depends essentially on the study of a sequence cf Laue photographs, the crystal being turned through a known number of degrees, by the help of a special two-circle goniometer, between the various exposures. The photographs are then analysed by the help of a new instrument termed a " cyclometer," and the direction of a structural plane of symmetry, if such be present, is thereby located. Fresh exposures on the goniometer lead to a determination of the " X-ray class of symmetry," that is, the real class to which has been added a centre of symmetry; and a set of crystal-elements can also be deduced. In other words, the investigation can be evidently carried to the same stage as is custom-

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[1] P. Niggli, " Geometrische Krystallographie des Diskontinuums," 1919, a book that arose from an analytical investigation of the cubic-point system by the same author, *Jahrb. Min. Beil-Bd.*, 1919, **43**, 1.

[2] A. Sommerfeld, " Atombau und Spektrallinien."

[3] R. Gross, *Centr. Min.*, 1920, 52.

ary by orthodox geometrical methods, but the crystal need have no plane faces. The method has already been applied to crystals of tungsten,[4] and also, without an actual publication of details, to tridymite and hæmoglobin.

What appears to be a final determination of the symmetry-class of the mineral benitoite may well be mentioned here, as illustrating the meaning of the term X-ray class of symmetry. According to F. Rinne,[5] there are only three symmetry-classes which are worthy of a consideration : (1) trigonal equatorial, (2) ditrigonal equatorial, and (3) ditrigonal polar, each of which by addition of a centre of symmetry happens to lead to a distinct class, namely, (1) hexagonal equatorial, (2) dihexagonal equatorial, and (3) dihexagonal alternating. Laue photographs of homogeneous portions of a crystal unmistakably rule out the first and third alternatives, and benitoite is accordingly the first representative of the ditrigonal equatorial class.

Theoretical discussions of the finer details of crystal structure are becoming more frequent. The effect of various possible types of electronic arrangement on the general symmetry of the diamond, rock-salt, and sylvine has been worked out by H. Thirring.[6] With regard to the much-vexed question of the chemical aspect of crystal structure, opinion would seem to have taken a welcome, if belated, turn in the German literature—perhaps on account of Willstätter's [7] expressed opinion that the disappearance of the molecule in a crystal cannot be reconciled with the immense body of well-established facts of organic chemistry. Two papers by A. Reis [8] are also suggestive in this connexion. An allusion may also be made here to the important work, which has been carried on during the last twenty-five years, on the behaviour of crystals to infra-red radiation—work that is disseminated in various journals and worthy of a complete Report in itself. In a sense, the work has more chemical interest than X-ray work, for infra-red radiation would seem to be a molecular as opposed to an atomic probe. All carbonates, for example, exhibit an intense reflection for infra-red rays of a specific wave-length, no matter whether they are in the state of fusion, solution, or crystal. Quite recently there have been numerous attempts to correlate the extreme wave-lengths (residual rays—" Reststrahlen "), selectively reflected by crystals, with the elastic and other constants. An important paper by H. Rubens and H. von Wartenberg [9] is the key to

[4] R. Gross and N. Blassman, *Jahrb. Min. Beil-Bd.,* 1919, **42,** 728.

[5] *Centr. Min.,* 1919, 193.

[6] *Physikal. Zeitsch.,* 1920, **21,** 281 ; *A.,* ii, 477.

[7] R. Willstätter, *Zeitsch. angew. Chem.,* 1919, **32,** 331.

[8] *Zeitsch. Elektrochem.,* 1920, **26,** 408, 412.

[9] *Sitzungsber. Preuss. Akad. Wiss. Berlin,* 1914, 189 ; *A.,* 1914, ii, 236.

some of the earlier papers. Some supplementary references[10] to more recent papers may be useful to those who are interested. It must be noted that the conclusions about fluorspar are vitiated by an arithmetical mistake. An early publication of the new computations is promised.

As the portion devoted to Mineralogy is supposed to cover a period of three years, it will be realised that no space can be allotted to the results of chemical analysis and descriptions of new mineral species; further, that little attention can be devoted to what may be termed the observational side of the science. Fortunately, these aspects are already well cared for in special journals. A recent list of new minerals, for example, has been given by Spencer,[11] and a new venture on the part of the *Mineralogical Magazine*—the publication of abstracts—would seem to be justified by results. Several important American investigations of mineral systems are to be noted, which emphasise the desirability of the foundation on this side of something of the nature of a Petrophysical Institute; which, without being an exact copy of the American original, could fruitfully co-operate with it in the advancement of pure and applied science. Without some such centre there are almost insuperable difficulties in the way of any serious European contributions to experimental mineralogy, for the problems there involved require such special resources as are scarcely within the power of a University laboratory to provide. One department of such an Institute might well be devoted to the manifold chemical problems connected with crystals. The future of crystallo-chemical analysis, in particular, would seem to require something more than the spasmodic support of individuals. The simplification of the method, and the reduction to a unified system of the numerous compounds described within the last six years, not to speak of the limitless compounds of the future, would require some form of organised effort. Chemists could then be encouraged, not only to send their new crystalline compounds to be investigated and registered, but also to expect help, as a matter of course, in the identi-

[10] H. Rubens, *Ber. Deut. physikal. Ges.*, 1915, **17**, 315; *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1917, 43; H. P. Hollnagel, *Physical Rev.*, 1918, **11**, 135; M. Born, "Dynamik der Kristallgitter," 1915; *Ber. Deut. physikal. Ges.*, 1919, **21**, 533; M. Born and O. Stern, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1919, **48**, 901; M. Born, *ibid.*, 1918, 604; *A.*, ii, 401; M. Born and A. Landé, *Ber. Deut. physikal. Ges.*, 1918, **20**. 210; *A.*, 1919, ii, 188; A. Landé, *ibid.*, 1918, **20**, 217; 1919, **21**, 644; K Fajans, *ibid.*, 1919, **21**, 539, 714; *A.*, ii, 21; M. Born, *ibid.*, 1919, **21**, 533; *Ann. Physik*, 1920, [iv], **61**, 87; *A.*, ii, 227; M. Born and E. Bormann, *ibid.*, 1920, **62**, 218; W. Voigt, *ibid.*, 1919, **60**, 638.

[11] L. J. Spencer, *Min. Mag.*, 1919, **18**, 373.

fication of complex products of reaction, especially in those cases in which they are hampered by a paucity of material.

Atomic Distances and Volumes.

Two recent attempts to carry our knowledge of atomic volumes beyond the stage represented by Lothar Meyer's well-known curve would seem to indicate substantial progress towards a solution of the simpler problems connected with this most difficult subject.

The first paper to be noted deals not so much with volumes as with atomic distances in crystals. As a result of a critical survey of the numerous structures which have been successfully determined by various X-ray workers, W. L. Bragg[12] finds that the distance between contiguous atomic centres of any given pair of elements, A and B, is almost constant for all crystals. Now, if the atoms be regarded as spherical, this distance can be regarded as made up of the sum of the radii of the two atoms, and if the radius of atom A be known then the radius of atom B can be obtained by subtraction. In this way, by making use of the X-ray data referring to such crystalline elements as carbon, silicon, and various metals, the author is subsequently able to deduce preliminary values for the atomic radii of such elements as oxygen, nitrogen, sulphur, and the halogens, which have so far only been investigated in the form of compounds. These preliminary estimates are then mutually adjusted by an elaborate series of cross-checks, the result being a table of mean radii or diameters, in agreement as a rule with individual observations within the limits ±10 per cent. Further, it is possible to deduce diameters for certain other elements from comparisons of the molecular volumes of isomorphous substances. The results are given in the form of a curve (with atomic diameters plotted against atomic numbers), which is here reproduced as far as the element strontium (see Fig. 1). It is seen that the diameters, as thus deduced from the established structures of crystalline elements and compounds, are of the same periodic character as the so-called atomic volumes of the Lothar Meyer curve. (Parenthetically, it may be here added that the ionic radii for the halogens and alkali metals have been deduced in another way by A. Landé,[13] who attributes a greater radius to a halogen ion than to an ion of the alkali metal immediately following it in the list of the elements. A similar view is held by K. Fajans.[14] This want of agreement between Bragg and Landé and Fajans cannot be discussed here, as the more important of the German papers are not available.)

[12] *Phil. Mag.*, 1920, [vi], **40**, 169 ; *A.*, ii, 537.

[13] *Zeitsch. Physik*, 1920, **1**, 191 ; *A.*, ii, 540.

[14] *Ibid.*, **2**, 309 ; *Zeitsch. Elektrochem.*, 1920, **26**, 502.

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Bragg's paper must be consulted for a discussion of the physical significance assigned to these diameters. The immediate object would seem to be strictly practical. " The way of regarding the atoms as spheres packed tightly together is useful in constructing models of crystalline structures . . . and, it is hoped, will help in future investigations . . . by limiting the number of possible arrangements." An example of this practical usefulness will be given below under cæsium dichloroiodide. The writer would also mention that the application of the method to the cassiterite group and to anatase [15] points to the need of a revision of the models which have hitherto been offered.

The second investigation refers to the volumes of elementary atoms. Setting out from the current view that the elements typified by sodium, magnesium, aluminium, and silicon respectively possess 1, 2, 3, and 4 outer electrons, and a corresponding effective

Fig. 1.
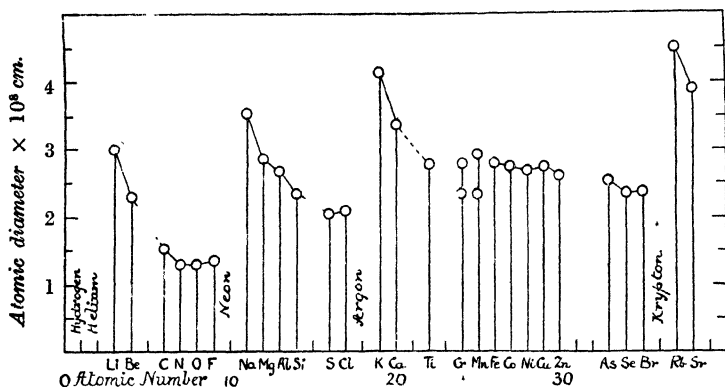
number of positive charges on the nucleus, Sommerfeld [16] examines the attractive effects of these successive increases in nuclear charge on the radius of the outer electronic ring, and he deduces that the atomic radii of the four elements specified should exhibit the ratios $1 : 0\cdot57 : 0\cdot42 : 0\cdot33$. He also points out (as will be indicated presently) that these values are in fair agreement with the values obtained by dividing atomic weight by specific gravity. Now W. L. Bragg has emphasised the fact that the structural details of a crystal must be taken into account; that the packing of spherical atoms is closer in some elements than in others; in other words, that the old meaning of atomic volume is of the nature of a fiction. It is therefore interesting to bring into the comparison the values of the true absolute volumes (for which the writer is responsible),

[15] *Ann. Reports*, 1917, **14**, 233.   [16] A. Sommerfeld, *op. cit.*, 105.

and also their ratios. The various results are embodied in the following table.

Table of Volume Constants.

	Na.	Mg.	Al.	Si.
Hull's absolute distances (2r)	3·72	3·22	2·86	2·35 × 10⁻⁸ cm.
True absolute " spherical " volumes..	26·9	17·5	12·2	6·79 × 10⁻²⁴ c.c.
True atomic-volume ratios	1·00 :	0·65 :	0·45 :	0·25
Sommerfeld's theoretical ratios	1·00 :	0·57 :	0·42 :	0·33
Sommerfeld's cited ratios........	1·00 :	0·57 :	0·41 :	0·51

It is seen that the true atomic-volume ratios are in general agreement with Sommerfeld's theoretical values, and do not exhibit the great discrepancy 0·51 with respect to silicon—an apparent but not a real anomaly, which is simply due to the relatively open packing of the silicon (or diamond) structure. The general agreement is no doubt due to the relative simplicity of the problem of atomic volumes in the particular case of chemically uncombined elements.*

Recent Structural Models.

In view of the novelty and high degree of importance attached to the X-ray method, an attempt has always been made in these Reports to give complete lists of those models which appear to be well established. This custom will be adhered to on the present occasion.

Some Cubic and Hexagonal Elements and Compounds.—There are some fifteen substances which can be disposed of in the form

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* A brief note on the more salient aspects of atomic volumes in compounds may not be out of place. It might seem at the outset that the conversion of W. L. Bragg's absolute " atomic diameters " into corresponding spherical volumes (whereby the fluctuations naturally become of the order ± 30 per cent.) might throw light on such a perplexing problem as the undoubted volume equality of ammonium and rubidium compounds—a problem to which neither atomic weights nor atomic numbers bring any solution. Now the radius of the ammonium radicle can scarcely be greater than the sum of the radius of nitrogen and the diameter of hydrogen. As the latter diameter is generally accepted by physicists to be 10⁻⁸ cm., the radius of the radicle comes out to be 1·65(× 10⁻⁸ cm.), which is much lower than 2·25, the radius of the rubidium atom. The corresponding spherical volumes are, of course, much further away from the expected ratio 1 : 1, being by calculation in the proportion 1 : 2·5. The nearest interpretation of this discrepancy is that an initially spherical or (as some mathematical physicists prefer) cubical atom suffers a deformation on entering into chemical union; but the obvious difficulties which stand in the way of any precise definition of the new shapes, added to the possibility that atoms may change their volume on combination owing to a rearrangement or an actual transfer of electrons, would seem to demand the discovery of new methods of experimentation before real progress can be made.

H* 2

of a table. With the exception of thorium and nickel (determined by H. Bohlin),[17] all the values given below are due to Hull,[18] who says, apropos cobalt : " A finely powdered sample produced by rapid electrolysis showed a mixture of cubic and hexagonal close-packing in nearly equal ratio. After annealing in hydrogen at 600°, this sample showed only the cubic form. Another sample, composed of filings from pure cast metal, showed slight traces of hexagonal packing, due presumably to straining. It is possible that the other close-packed metals will behave in a similar manner, but this question has not been studied." According to Hull, ductility in a metal is a result of a face-centred cubic arrangement.

Table of some Cubic and Hexagonal Structures.

	Arrangement of atoms.	Grating distance of cube planes.	Distance between atomic centres.
Cobalt (dimorphous)...	Face-centred cube (cubic close-packed).	1.785×10^{-8} cm.	2.52×10^{-8} cm.
Thorium	Do.	2·56	3·62
Nickel	Do.	1·765	2·50
Rhodium	Do.	1·91	2·70
Platinum	Do.	2·01	2·85
Chromium	Centred cube	1·455	2·52
Molybdenum	Do.	1·575	2·73
Magnesium	Hexagonal close-packed.	—	3·22
Zinc	Do.	—	2·84
Cadmium	Do.	—	3·15
Cobalt (dimorphous)...	Do.	—	2·53
Lithium fluoride*	Simple cube	2·01	2·01
Sodium fluoride*	Do.	2·31	2·31
Potassium fluoride* ...	Do.	2·69	2·69
Magnesium oxide* ...	Do.	2·11	2·11

* In these four cases the arrangement of like atoms is, of course, given by the face-centred cube.

Antimony.[19]—The nature of this structure is perhaps best grasped as follows. Suppose the familiar rock-salt cell, of Fig. 2, be set up with a solid diagonal vertical and then extended along it until the original cubic 90°-angle has attained the value 92° 53′. The edge of the cell must now be taken to be 3.10×10^{-8} cm.; the corresponding length of the vertical diagonal is 5·64. Now let the centres of the chlorine atoms be shifted through a vertical distance of 0·42 (exaggerated in Fig. 3), and finally suppose all the atoms to be replaced by antimony; the result is the antimony structure, which is the first example among elements of a "hexahedral" structure, that

[17] *Ann. Physik*, 1920, [iv], **61**, 421 ; *A.*, ii, 214.
[18] A. W. Hull. *Proc. Amer. Inst. Electrical Engineers*, 1919, **38**, 227.
[19] R. W. James and N. Tunstall, *Phil. Mag.*, 1920, [vi], **40**, 233 ; *A.*, ii, 548.

is, one in which each atom is closely environed by six other atoms. In all previous cases of elementary substances the environment has always been tetrahedral, octahedral, or dodecahedral.

Zincite,[20] ZnO.—The crystal structure of this well-known dihexagonal polar mineral provides one of the few cases in which a verbal description is better than a diagram. Isomorphous with greenockite, CdS, and wurtzite, ZnS, it exhibits an interesting structural contrast to the commoner form of zinc sulphide—zinc blende. In both minerals the zinc atoms are essentially arranged in accordance with the principle of close-packing, the difference being that in zinc blende the "cubic" style of close packing is affected, in zincite the "hexagonal" style. In both structures the zinc (or cadmium) atoms are environed tetrahedrally by the sulphur (or oxygen) atoms.

FIG. 2.   FIG. 3.

O = Na, ● = Cl.   O = Sb
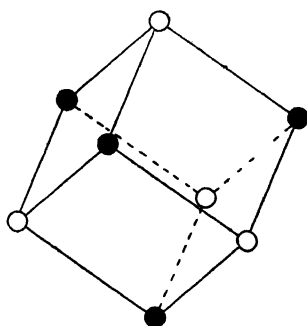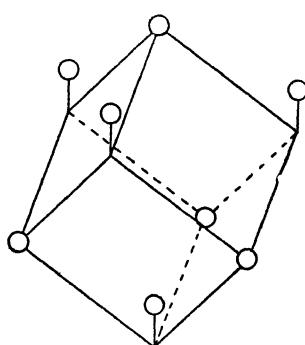
The absolute vertical distance in zincite between successive layers of similar atoms is 2·60, whilst the horizontal interval between adjacent atomic centres is 3·22. It is of interest to recall the fact that E. S. Fedorov [21] showed that two different structures are reconcilable with the preliminary observations recorded in W. H. and W. L. Braggs' well-known book, one of them demanding atomic polarity, the other being the structure finally adopted by W. L. Bragg.

The Calcite Group.—An X-ray study that has some bearing on the question of the existence of groups of atoms in crystals we owe to R. W. G. Wyckoff,[22] who has subjected calcite, rhodochrosite, chalybite. and magnesite (as also sodium nitrate [23]) to an investiga-

[20] W. L. Bragg, *Phil. Mag.*, 1920, [vi], **39**, 647 ; *A.*, ii, **433**.

[21] *Bull. Acad. Sci. Petrograd*, 1916, **10**, 377.

[22] *Amer. J. Sci.*, 1920, [iv], **50**, 317.

[23] *Idem.*, *Physical Rev.*, 1920, [ii], **16**, 149 ; *A.*, ii, **756**.

tion by the Nishikawa method—essentially an ingenious combination of the Laue and de Broglie methods. The nature of some of these compounds has been previously elucidated by W. H. and W. L. Bragg, who explained their results in terms of a face-centred lattice, but the structures are, perhaps, best visualised as being the sodium chloride structure, which has been deformed along a three-fold axis until the cleavage cube has acquired the angles of the cleavage rhombohedron, the sodium and chlorine atoms being then regarded as substituted by calcium atoms and carbonate groups respectively. An inspection of Fig. 4 (which is drawn true to scale) will show that triads of oxygen atoms are relatively close to individual carbon centres. The main result of the new investigation is to show that these triads are at a constant distance of 1·22 Ångström units from their corresponding carbon atoms, although all other atomic distances vary considerably in passing from one car-

FIG. 4.	FIG. 5.
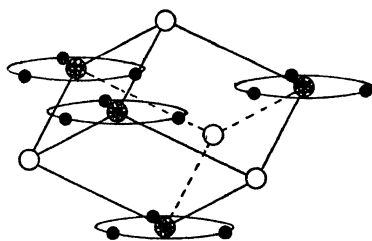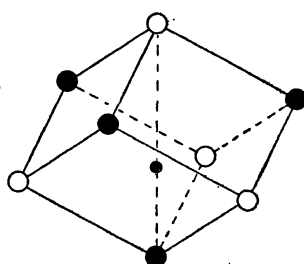
O = Ca, ⊕ = C, ● = O.   O = Cs, ● = I, ● = Cl.

bonate to another—the distances between adjacent carbon and metallic atoms, for example, being 3·04 and 2·83 Å.U. in calcium and manganese carbonates respectively. This can be interpreted as evidence of the persistence in the crystal structure of the CO_3-groups, the internal details of which are, so to speak, no concern of the externally placed metallic ion.

Caesium Dichloroiodide, $CsCl_2I$.—The elucidation of this rhombohedral substance has been successfully accomplished by the same author [24] by means of the Nishikawa method. The lattice can be regarded as derived from the rock-salt type of structure, by a compression along a three-fold axis, until the cubic 90° angle has acquired the rhombohedral 80° 12′ value. The absolute dimension of this vertical length is $6·06 \times 10^{-8}$ cm.; cæsium and iodine atoms are placed alternately at the corners. A chlorine atom is located

[24] R. W. G. Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1100 ; *A.*, ii, 489.

on the principal axis of this cell at a distance equal to 0·62 times the cell-diagonal, from either the cæsium or the iodine atom.* The origin of this ambiguity lies in a circumstance peculiar to the chemical composition; the reflecting powers of the horizontal strata of cæsium and iodine atoms are approximately equal (on account of the close atomic weights or numbers of the elements concerned), and the strata are accordingly indistinguishable from each other by means of X-rays. . . . The writer therefore thought it would be interesting to examine the two questions: (1) whether the structure as determined by Wyckoff is reconcilable with W. L. Bragg's values of atomic diameters, and (2) whether the application of these atomic diameters serves to remove the ambiguity concerning the position of the chlorine atoms. The answers to both these questions would seem to be emphatic affirmatives. Figs. 6—7 represent
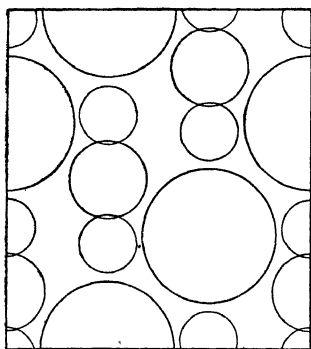
FIG. 6.   FIG. 7.
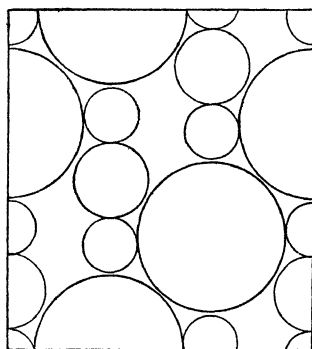
vertical elevations on the plane ($\bar{1}10$). In Fig. 6 W. L. Bragg's mean values, $Cs = 4·74$; $I = 2·80$; $Cl = 2·10$, have been adopted; although there is a slight interpenetration of the iodine and chlorine spheres of influence, the spacial accommodation for the various spheres can be regarded as satisfactory. This interpenetration can be avoided and the general fit improved, without tampering with Wyckoff's data, if some such amended values as $Cs = 5·36$, $I = 2·70$, and $Cl = 1·90$ be adopted (compare Fig. 7). In both figures the chlorine-centres have been taken as lying nearer to iodine than to cæsium; if the chlorine-centres lay nearer to cæsium, they would fall inside the cæsium atoms.

* Since each of the corner-atoms of the cell is really common to eight cells in an infinitely extended structure, and since the chlorine atom belongs wholly to the cell illustrated, it follows that the total cell-composition is $\frac{1}{8}(Cs_8I_4)Cl$, which is equivalent to $CsICl_2$.

Physical Crystallography.

This important branch of physics is poorer by the loss of Professor W. Voigt, of Göttingen, so celebrated for his experimental researches in elasticity and the many other abstruse properties of crystals requiring a highly mathematical treatment.

Electrolytic Conduction.—The many experimental difficulties which have long stood in the way of an exact study of electrolytic conduction in crystals have been recently overcome by Tubandt,[25] who has thereby opened up a new field of investigation (the abstract must be consulted for an account of the general method of experimentation). Since the specific conductivities of the compounds examined are very low at ordinary temperatures, the experiments were carried out in a stream of an indifferent gas at as high a temperature as practicable. This immediately led to the interesting observation that the specific conductivity of the cubic form of silver iodide (stable above 144·6°) is 3000 times as great as in the case of the hexagonal modification (both measured near the transition temperature), and if the measurement be effected close to the melting point the value is actually much higher for the solid than for the fused substance. Crystals of silver chloride, bromide, and iodide were found to behave as unidirectional electrolytes, permitting freely the migration of silver ions (in amounts which rigorously obey Faraday's law), but preventing all movement of halogen ions in the reverse direction. Lead chloride, however, behaves in exactly the opposite way, the negative chlorine ions migrating freely. The author points out that these trustworthy results of careful experiment are difficult to reconcile with a view that the crystal ions of binary compounds are held in equilibrium by electrostatic forces. The investigation of silver sulphide, of which there are two forms, $\beta \rightleftharpoons (179°)a$, revealed a new point of interest. The high temperature a-modification behaves just like the halogen salts of silver, but with the β-form there is simultaneously an electronic conduction in the opposite direction, so that the crystal exhibits both electrolytic and metallic conduction. The author is disposed to refer this to the presence in the β-form of two kinds of molecules.

Ultramicroscopic Inclusions in Crystals.—It will be remembered that inorganic ultra-microscopic "colloidal" particles have been definitely proved to be crystalline by the use of the Debye-Scherrer-Hull method of X-ray exploration.[26] The investigation of minute

[25] C. Tubandt, *Mitt. Naturforsch. Ges. Halle,* 1917, **4,** 21 ; C. Tubandt and S. Eggert, *Zeitsch. anorg. Chem.,* 1920, **110,** 196 ; *A.,* ii, 279 ; C. Tubandt, *Zeitsch. Elektrochem.,* 1920, **26,** 360.   [26] *Ann. Reports,* 1919, **16,** 197.

particles in crystals by the help of the ultramicroscope is now proceeding. The beginnings of this work apparently lie in a suite of papers [27] on the nature of metal-fogs in crystals. It has been found that absolutely pure crystals of lead chloride, silver chloride, and bromide (that is, crystals of the ordinary substances which have been recently treated with halogen to transform any trace of free metal into haloid) are ultramicroscopically transparent. If this material is melted and treated with a trace of free metal or of a reducing agent like potassium cyanide, a metallic fog is produced in the re-solidified material. Novel results are obtained in the case of lead chloride, for owing to the strong double refraction of the crystal each speck of light, arising from an ultramicroscopic particle, is doubled and plane-polarised. Thallium chloride and bromide could not be obtained clear, since they cannot be treated with halogen without the formation of higher haloids.

The method has been more recently applied [28] to a study of the origin of opalescence in mixed crystals of sodium and potassium chloride, occasionally erupted by Vesuvius. The previous investigation of the binary system, NaCl–KCl by Nacken [29] was, of course, invaluable. The opalescence is due to a separation of the two components consequent on the temperature falling below the point of complete miscibility for a given mixture. It was instructive to observe the process in laboratory products of various compositions, as it gradually unfolded itself under the ultramicroscope. The crystal becomes' doubly refracting, due to strains; then the separated particles reveal their existence, and finally strains and the double refraction disappear. The author proposes to attack the system orthoclase–albite, in which a primary homogeneous mixed crystal ("anorthoclase") will no doubt eventually yield a micro- or cryptoperthitic structure.

Specific Heats of Minerals.—A monumental research on the specific heats of the various modifications of silica and of the more important silicates has been published by White,[30] who within the last few years has greatly improved the general technique of high temperature measurement. The constants directly determined were "interval-specific heats," that is, average specific heats over such ranges of temperature as 0—100°, 0—300°, 0—500°, and so on. From these values the specific heat at any desired temperature was deduced by two new methods, which gave perfectly consistent

[27] R. Lorenz and W. Eitel, *Zeitsch. anorg. Chem.*, 1915, **91, 46, 57, 61**; *A.*, 1915, ii, 260.

[28] W. Eitel, *Centr. Min.*, 1919, 173.

[29] R. Nacken, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1918, 192; *A.*, 1919, ii, 281.

[30] W. P. White, *Amer. J. Sci.*, 1919, [iv], **47**, 1; *A.*, 1919, ii, 133.

results, and this when multiplied by the factor M/n (where M is the molecular weight, and n the number of atoms in the molecule), finally yields the mean atomic heat. At the ordinary temperature the value of the last-mentioned constant is of the order 3·3 for silica and 3·75 for silicates; it increases with rise of temperature, at first quite rapidly and then more gradually as it approaches a limiting value in the neighbourhood of 6·0. The results will no doubt have great significance in the future study of certain geological processes, but it may be noted that they have already an important bearing on various questions of great theoretical interest. The atomic heat at constant volume, for example, can be computed from the observed atomic heat at constant pressure by the help of a well-known thermodynamic formula, involving compressibility, thermal expansion, and density, but the computed value for cristobalite (according to Fenner [31] the stable modification of silica above 1470°) cannot be reconciled with generally accepted theoretical ideas, which must accordingly rest on a faulty basis. Moreover, the results obtained from a study of the various modifications of silica can be used as a test of the reasonableness of Smits' theory of dynamic allotropy,[32] and as a result of his painstaking work of precision the conclusion is drawn by White that it is possible to over-estimate the value of that theory.

Optics.—Attention must be called to a paper [33] on the general optical properties of amyrolin, $C_{14}H_{12}O_3$. This monoclinic substance exhibits an abnormally high birefringence (apparently only exceeded by calomel), and is also very noteworthy on account of a strong dispersion of the conical refraction. Two papers by A. Ehringhaus [34] on the dispersion of the birefringence of many substances are also worthy of a careful perusal.

Comparative Chemical Crystallography.

The progressive nature of the effects produced by a mutual substitution of the elements potassium, rubidium, and cæsium, as well as the close similarity of rubidium and ammonium compounds, which has been largely emphasised by Tutton's investigations during the last thirty years, is now so well known that it is only necessary to place on record a recent paper by this indefatigable worker [35] dealing with the compounds typified by the formula

[31] C. N. Fenner, *Trans. Soc. Glass Technology*, 1919, **3**, 116.
[32] *Ann. Reports*, 1914, **11**, 258.
[33] H. Rose, *Jahrb. Min.*, 1918, 1 ; *A.*, 1918, i, 26β.
[34] *Ibid., Beil.-Bd.*, 1916, **41**, 342 ; 1920, **43**, 557.
[35] A. E. H. Tutton, *Proc. Roy. Soc.*, 1920, [A], **98**, 67 ; *A.*, ii, 690.

$R_2Cu(SeO_4)_2,6H_2O$. There are also two papers to be noted referring to series of organic compounds. The first, by A. Ries,[36] deals with an extensive series of mono-, di-, tri- and tetra-alkyl derivatives of ammonium picrate, some of which have been previously examined by Jerusalem. The main results of this work are two in number: first, the prevalence of polymorphism in organic compounds (many of the substances appearing in three or four forms), and secondly, the regularity with which one of the modifications of every tetra-substituted picrate is either strictly hexagonal or pseudo-hexagonal. The theoretical interpretation of this regularity would have been easy if the substances concerned had been tri-substituted. The second paper [37] deals with the series of compounds, typified by the general formula $R_4N \cdot HgI_3$, in which R represents various alkyl, aryl, or alphyl groups. One result is to prove that the racemic compound, dl-Ph(CH$_2$Ph)MeEtNHgI$_3$, is isomorphous with the corresponding diethyl compound, which necessarily consists of identical and symmetrical molecules. Perhaps the most noteworthy features of the paper, however, are the omission of all computed angles, as being unnecessary to any future purpose, and also the description of the methods devised in recent years, which serve to reduce the routine work of crystal description to about one-third of that formerly required.

Methods of Investigating Opaque Substances.

Although opaque minerals are not relatively very numerous, they represent a highly important class of compounds, if only because of their supreme economic value. In the past the identification of opaque compounds has had to depend on such simple physical tests as density, cleavage, hardness, and streak (supported by the methods of chemical analysis), since the ordinary optical methods are only applicable to transparent substances; but in recent years more and more attention has been paid to those special microscopic methods introduced by Sorby, which have been developed more and more in connexion with metallography. This technique has been applied to minerals (notably in America). The new method has been recently expounded in at least two books,[38, 39] and a general account, together with a most valuable bibliography, has also been

[36] *Zeitsch. Kryst. Min.*, 1920, **55**, 454; *A.*, i, 715.

[37] T. V. Barker and (Miss) M. W. Porter, *T.*, 1920, **117**, 1303.

[38] J. Murdoch, "Microscopical Determination of the Opaque Minerals," 1916.

[39] W. M. Davy and C. M. Farnham, "Microscopic Examination of Ore Minerals," 1920.

given by a German worker.[40] The method has been variously named "Mineralography," "Opakography," and "Mineragraphy"—terms which are perhaps less pronounceable than "Chalcography" (suggested by Brauns).

The method consists essentially of the examination, under a microscope fitted for side-illumination, of the upper surface of a specimen which has been ground, polished, and possibly etched with various reagents. Both ordinary and plane polarised light are employed. In the latter case any opaque mineral that does not belong to the cubic system may reflect two plane or elliptically polarised rays, one of which is somewhat retarded (not, in general, to the same extent as in the case of transparent substances). The principles underlying the various optical effects have been recently treated very thoroughly by Wright,[41] who has also done much to perfect the finer technique.[42] The method has obviously a great future, not least on the purely scientific side, for it promises to lead to a revision of many opaque mineral species. It should also prove useful in the examination of dyes and lakes.

Thermal Studies of Mineral Systems.

Thermal studies of mineral systems are becoming so numerous that they cannot all be described with a fullness proportionate to their deserts. In making a selection, the writer is compelled to restrict himself to some relatively simple investigations, and, inferentially, to omit any consideration of the complex ternary system,[43] $CaO-MgO-SiO_2$, as also of Niggli's work [44] on certain mixed fusions involving the oxides of sodium, potassium, calcium, aluminium, carbon, silicon, and titanium. It is believed that the relatively simple cases will give a general idea of the significance of the present-day type of work, which is presumably the main object of this Report.

Binary Systems involving Barytes, Celestine, and Anhydrite.— In continuation of his previous work,[45] in which it was proved that barytes, celestine, and anhydrite pass into other modifications (probably monoclinic) at high temperatures, Grahmann [46] has investigated the miscibility relations of the substances over a vast

[40] H. Schneiderhöhn, *Jahrb. Min. Beil.-Bd.*, 1920, **43**, 400.
[41] F. E. Wright, *Proc. Amer. Phil. Soc.*, 1919, **58**, 401.
[42] *Idem, Mining and Metallurgy*, 1920, No. 158.
[43] J. B. Ferguson and H. E. Merwin, *Amer. J. Sci.*, 1919, [iv], **48**, 81, 165; *A.*, 1919, ii, 401, 459.
[44] P. Niggli, *Zeitsch. anorg. Chem.*, 1916, **98**, 241; *A.,* 1917, ii, 211.
[45] *Ann. Reports*, 1913, **10**, 256.
[46] W. Grahmann, *Jahrb. Min.*, 1920, i, 1.

range of temperatures. The method adopted was that of cooling curves, supplemented by density determinations and by a study of the optical properties in thin sections. It is found that each pair of the α(high temperature)-modifications yields an uninterrupted series of mixed crystals. This is also true for the β(low tempera-ture)-modifications of barium and strontium sulphates—in other words, for barytes and celestine. On the other hand, the misci-bility of the β-modifications of calcium and strontium sulphates (anhydrite and celestine) is limited even at the high temperature of 1000°, and becomes more restricted at the ordinary temperature. Anhydrite can take up 42 mol. per cent. of strontium sulphate, and celestine up to 12 per cent. of calcium sulphate—the mixtures being isodimorphous in Retgers' sense. Anhydrite and barytes present a similar behaviour, but the miscibility is much more restricted, each being able to take up about 6 per cent. only of the other. The research is, of course, of considerable mineralogical interest, for it reveals miscibility possibilities far in excess of those actually observed in nature, as determined by mineral analyses.

Binary System Åkermanite–Gehlenite.[47]—The investigation of mixtures of these two compounds may be regarded as an excellent example of the experimental method of studying a perplexing mineral problem. Two distinct species—gehlenite,

$$3CaO,Al_2O_3,2SiO_2,$$
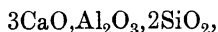
and melilite, $Na_2O,11(Ca,Mg)O,2(Al,Fe)_2O_3,9SiO_2$—are usually recognised as belonging to the tetragonal "melilite group." With these must be reckoned the closely related åkermanite, an impor-tant constituent of furnace slags, which, according to Vogt, is essen-tially a calcium silicate, $4CaO,3SiO_2$. Now a well-defined com-pound, $2CaO,MgO,2SiO_2$, was found by Ferguson and Merwin to play an important rôle in the ternary system, $CaO–MgO–SiO_2$, and they concluded it to be åkermanite in its purest form; moreover, since a compound, $2CaO,Al_2O_3,SiO_2$, deemed to be pure gehlenite, had been previously prepared by Rankin and Wright, the investi-gation of the equilibrium relationships of gehlenite and åkermanite suggested itself as a method of attacking the difficult problem of the melilite group. It is found that the two isomorphous compon-ents form an uninterrupted series of mixed crystals exhibiting a minimum melting point (Roozeboom's type III). As gehlenite and åkermanite are respectively negative and positive optically, one of the mixtures (55 per cent. of åkermanite) is isotropic. (As a matter of fact, this inversion of optical character was observed by Vogt in the case of certain furnace slags, which he regarded as

[47] J. B. Ferguson and A. F. Buddington, *Amer. J. Sci.*, 1920, [iv], **50**, 131 ; *A.*, ii, 621.

mixtures of gehlenite and åkermanite.) Another interesting item is that åkermanite glass has a higher density and refractive index than the crystalline modification. The authors hope to continue their work, so auspiciously begun, and there can be little doubt that the correct interpretation of the melilite group will not be long delayed.

Ternary System,[48] $MgO-Al_2O_3-SiO_2$.—The investigation of this system was beset with much difficulty owing to the high temperatures involved, which were frequently beyond the limits of the platinum furnace. The various binary compounds have been elucidated in previous researches and noted in these Reports. The only ternary compound is apparently a simplified cordierite,

$$2MgO,2Al_2O_3,5SiO_2,$$
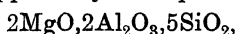
a phase which decomposes at a temperature lower than its melting point, but which can crystallise out of a complex mixture at somewhat lower temperatures. The compound is best prepared by holding a glass of like composition at temperatures lying between $900°$ and $1400°$; an unstable form begins to appear at $900°$, which goes over at a somewhat higher temperature to the stable form. The equilibrium relationships of this cordierite are somewhat complicated by the fact that it forms solid solutions with spinel, $MgAl_2O_4$, and sillimanite, Al_2SiO_5. Natural cordierite contains water, and part of the magnesia is replaced by ferrous oxide, but the general similarity in optical properties is sufficiently close to establish its identity with the synthetic, iron-free cordierite.

The Dehydration Process in Crystals (" Efflorescence ").

The results of a comprehensive investigation of this process have been recently published by Gaudefroy.[49] Although not generally susceptible to ocular proof under the microscope, loss of water is almost certainly accompanied by a temporary local liquefaction. By way of a general support to this conclusion, Gaudefroy states that almost any finely powdered hydrate can be transformed into a coherent cake by simply allowing it to remain in a desiccator for a few hours. This behaviour he attributes to a temporary solution of the solid in the water which it is about to lose by evaporation. In at least one case a periodic liquefaction and solidification is directly observable under the microscope. Under certain conditions a crystal of the heptahydrated zinc sulphate becomes covered with monoclinic crystals of the hexahydrated salt, which extend their

[48] G. A. Rankin and H. E. Merwin, *Amer. J. Sci.*, 1918, [iv], **45**, 301 ; *A.*, 1918, ii, 199.

[49] C. Gaudefroy, *Bull. Soc. franç. Min.*, 1919, **42**, 284.

boundaries in a rhythmic manner. At various stages a tiny crystal of the hexahydrate is surrounded by a zone of liquefaction, into which it grows as water is eliminated. The loss of one molecule of water of crystallisation is accompanied by a contraction equal to about one-tenth of the original molecular volume; and the surface of the new crystal consists of a concentric system of furrows and ridges as a result of this periodic shrinkage.

Another general point of interest is that the inception of dehydration and consequently the local formation of a dehydration figure can be readily brought about by inoculation with a fragment either of the actual product of dehydration or of a substance isomorphous with it. Thus if an orthorhombic crystal of magnesium chromate, $MgCrO_4,7H_2O$, be simply touched by a crystal of the anorthic copper sulphate, $CuSO_4,5H_2O$, dehydration of the chromate to the pentahydrate begins immediately, and proceeds at such a rate as to be visible to the naked eye.

Many hydrated substances lose water of crystallisation in more than one well-defined stage. To each stage there corresponds a characteristic dehydration figure. Thus, ferrous sulphate, $FeSO_4,7H_2O$, either loses three molecules of water or one; in the former case the figures are elliptical, whilst in the latter case the boundaries are rectilinear, being, in fact, either triangles or trapezia. With many substances two or more kinds of transformation take place simultaneously, so that it becomes impossible by means of a chemical analysis to correlate each type of dehydration figure with the specific amount of water lost. There are, however, other ways of deducing the composition of the different products. Thus the heptahydrated cobalt sulphate, unlike its isomorph ferrous sulphate, does not give the elliptical type of dehydration figure, but only the rectilinear type, and as the product can be proved by chemical analysis to be the hexahydrate, the same must be reasonably true of the corresponding type of figure given by ferrous sulphate. A confirmatory test is to drop small fragments of the dehydrated salt into a saturated solution of another salt; if the fragments grow isomorphously, their composition is thereby satisfactorily determined. This test is particularly trustworthy in the case of the vitriols, which have been so thoroughly investigated by previous workers from almost every conceivable point of view.

Following is a brief summary of the various types of dehydration figure revealed by Gaudefroy's researches.

Rectilinear Figures Determined by the Crystals under Dehydration.—Figures of this class are quite numerous, being, in fact, given in 54 per cent. of the substances examined. The dehydration takes place most favourably along certain selected planes of the

structural lattice, with the result that the dehydration figures on any given face are bounded by traces on that face of other important structural planes. By a study of the forms of the dehydration figure on the best developed faces of a crystal the "dehydration-polyhedron" can be determined, from which the dehydration figure for any other face can be deduced in the usual way. In the case of the monoclinic heptahydrated sulphates of iron and cobalt, the dehydration polyhedron is bounded by the forms {001}, {110}, and {10$\bar{1}$}. The material within the boundaries of a given dehydration figure is at first limpid, but soon becomes opaque; during the limpid stage it can be proved optically to consist of an irregular arrangement of minute crystals.

Rectilinear Figures Determined by the Product of Dehydration. —Each of these figures, in their simplest form, represents a single crystal of the new hydrate. The figures on any given face have accordingly no precise orientation. A good example is the hexahydrated decomposition product of ordinary zinc sulphate, which has already been mentioned as growing rhythmically.

Figures Exhibiting a Division into Four Sectors.—These are especially common in gypsum, the anorthic and orthorhombic vitriols, and the ferrocyanides. Opposite sectors are optically similar. The diagonals of the sectors are generally more distinct than the external boundaries, and have a definite orientation on each crystal face. The fine structure of the sectors is sometimes very complicated, but as a rule each sector is made up of a parallel bunch of fibres.

Elliptical Figures.—These figures are characterised by an extraordinarily fine texture of component particles arranged with every possible orientation. The figures are generally very deep-seated, and the internal surfaces are also curved. Wherever several kinds of dehydration figure are given by the same substance, the elliptical figures are characteristic of that chemical change which involves the greatest loss of water, and the excessively minute size of the component particles is attributed to the powerful disruptive effects of the correspondingly great contraction of molecular volume. It is interesting to note that the ratios of the ellipsoidal axes may differ widely in isomorphous substances. In zinc vitriol, for example, the ratios are $1\cdot1:1:1\cdot4$, whilst in the corresponding magnesium salt the ellipsoid practically becomes a sphere, and the figures on all the faces are substantially circles and not ellipses. In a monoclinic crystal one of the three ellipsoidal axes is always coincident with the symmetry axis, and in a uniaxial crystal the ellipsoid is one of rotation.

T. V. BARKER.

RADIOACTIVITY.*

Nuclear Constitution of Atoms.

THE nuclear theory of the atom is based on the form of the trajectory of the α-particle in passing through the atom, which in turn is deduced from the deviation suffered by the α-particle in its passage.[1] The fact that the overwhelming majority of the α-particles pursue practically rectilinear trajectories, whilst a few of them are deviated more or less abruptly, led to the well-known conception of the atom as a system of sparsely distributed single electrons occupying the atomic volume, equal in number to the atomic number of the atom, with a concentrated countervailing positive charge, equal in magnitude to the combined charge of the electrons, at the centre of the atom, and constituting a nucleus of dimensions excessively small relatively to the atomic volume. The inference that this nucleus contains all but some 0·05 to 0·02 per cent. of the mass and weight of the atom follows from the known mass of the contained negative electrons, and is in general accord with the electrical theory of mass. According to this, the mass of an electric charge is proportional to the square of the charge and inversely proportional to its diameter. To account for its mass on this view, the diameter of the nucleus of the uranium atom would be 4×10^{-15} cm., or 1/50th of the diameter of the single negative electron, if it consisted of pure positive electricity. That the nucleus is not a pure positive charge, but contains negative electrons, the net charge being positive and equal to the atomic number, is shown by the emission of β-rays from the radio-elements and by the mode of formation of isotopes in radioactive changes. Hence the view is not free from inconsistencies.

Impact of α-Particles on Heavy Atoms.—Great improvements have been made in the comparison of the experimental results of scattering with the mathematical theory. The magnitude of the

nuclear charge for platinum, silver, and copper has been evaluated accurately by a determination of the ratio of α-particles scattered over a solid angle between 22° and 36·5°. This ratio is proportional to the square of the atomic number and a quantity depending on the velocity and known physical and instrumental constants. The minuteness of the ratio makes a direct determination, by comparing the number of α-particles scattered with those in the original beam, difficult. The difficulty was ingeniously overcome, however, by introducing a notched rotating disk into the path of the α-particles, when counting the direct beam, and so reducing them in a known ratio at will to a number comparable with the number scattered. In this case one obtains intermittent gusts of scintillations with any desired interval between, conditions which are very favourable to counting, and actually enable the number per second capable of being counted accurately to be five times as great as without the device. This is apart from the complete control over this number by varying the relative size of the notch.

The experimental values for the three metals named, 77·4, 46·3, 29·3, are, in each case, within the known probable error of the accepted values of the atomic numbers, 78, 47, and 29. This, incidentally, is an important confirmation of the correctness of the absolute magnitude of the atomic numbers, and shows that the Periodic Table contains no unsuspected vacant places.

With the same arrangements, it was possible to verify accurately the inverse-square law of force over the region in which scattering of the α-particle occurs for the platinum atom. The number of particles scattered, other conditions being constant, depends on the initial velocity of the α-particle raised to the power $4/(1-p)$, when the force around the nucleus deviating the particle varies as $1/r^p$, r being the distance. The experimental value of p found was between 1·97 and 2·03, a variation from the inverse-square law within the counting error of 4 per cent. The actual least distance of approach to the nucleus was between 7 and $14(\times 10^{-12}$ cm.) for high and low velocity α-particles respectively. From other experiments in this field and in that of the wave-lengths of the K-series of X-ray spectra, it follows that the inverse-square law holds over a range between 3 and $100(\times 10^{-12}$ cm.), and that there can be no electrons in this region in the case of a heavy atom like platinum. These are fundamental conclusions.[2]

Impact of α-Particles on Light Atoms.—Turning now to impacts of α-particles with the nuclei of light atoms, where the nucleus struck is violently repelled,[3] and itself constitutes a new type of

[2] J. Chadwick, *Phil. Mag.*, 1920, [vi], **40**, 734.
[3] *Ann. Reports*, 1914, **11**, 274 ; 1916, **13**, 261.

radiant particle, such as the H-particle resulting from the passage of α-rays through hydrogen, most striking results have been achieved. Here the α-particle approaches within $0.25(\times 10^{-12}$ cm.) of the hydrogen nucleus, and the results point to rapid changes and possibly to variations of the direction of the field of force within the distance 0.35. The inverse-square law no longer holds. Only one in 10^9 of the hydrogen atoms penetrated by the α-particle is repelled with a velocity sufficient to enable it to be detected beyond the range of the α-rays, or one H-particle is produced by a hundred thousand α-particles passing through 1 cm. of hydrogen gas at N.T.P. This number, though minute, is from ten to thirty times that to be expected if the inverse-square law held. The absorption of these H-particles over their range, which is four times that of the α-particle producing them, is reminiscent of the absorption of α-particles themselves, and is totally different from what is theoretically to be expected. With H-particles generated by long-range α-particles, over a range equivalent to 22 cm. of air, there is practically no diminution of the number of H-particles, whilst between this and the end of the range, 28 cm., there occurs a gradually increasing diminution. With H-particles generated by short-range α-particles, the theoretical curve is more nearly approached. The H-particles in the first case appear to be projected in the same direction as that in which the α-particle is travelling, or within a few degrees of it, all at the same velocity. It is clear that to this case, where a very intimate approach of the helium and hydrogen nuclei occurs, special considerations apply.[4]

The identity of these H-particles with hydrogen was proved by a determination of the deviation suffered in electromagnetic and electrostatic fields. The value of e/m found, 10^4, is in perfect accord with that of the hydrogen ion, 9570 (E.M.U.). Its velocity, namely, 1.6 times that of the α-particle generating it, is in perfect agreement with the maximum value calculated for a "head-on" collision. The charge is positive in sign, and no negatively charged particles were observed.[5]

With regard to light gases other than hydrogen, helium gives no particles differing in range from the generating α-particle. From this it is inferred that singly charged atoms of helium, the estimated range of which would be four times that of the α-particle, are not formed. But oxygen, nitrogen, air, and carbon dioxide all gave scintillations of similar brightness over a range of 2 cm. of

4 (Sir) E. Rutherford, *Phil. Mag.*, 1919, [vi], **37**, 537 : *A.*, 1919, ii, 256 L. B. Loeb, *ibid.*, **38**, 533 ; *A.*, ii, 145.

5 (Sir) E. Rutherford, *ibid.*, 562 ; *A.*, 1919, ii, 258.

air beyond that of the range of the generating α-particles. The number was of the same order as those obtained in hydrogen gas. The range, 9 cm. of air, was only one-third as great, and the brightness of the scintillations, at a distance equivalent to 7·5 cm. of air, was equal to that of an α-particle at 1 cm. from the end of its range, instead of at 0·5 cm., as for the H-particle. The original presumption,[6] that these short-range particles were due to atoms of oxygen and nitrogen carrying unit charge, has now been shown to be at fault.[7] It has been found possible to determine their nature by special arrangements for the examination of their deflexion in a magnetic field, allowing the use of wide slits. Instead of the particles from oxygen being less deflected than the generating α-particles,. as should be the case if they were singly charged atoms of oxygen, they were more deflected, which excludes the possibility that they can be oxygen atoms, either singly or doubly charged. A mass intermediate between 1 and 4 and a double charge were indicated. The deviation suffered was estimated to be 5 per cent. less than that suffered by H-particles in a direct comparison, and the conclusion was drawn that they consist of doubly charged positive particles of mass about 3 with a velocity 1·2 times that of the generating α-particle. There was no noticeable difference between oxygen and nitrogen, so far as these short-range particles are concerned. Both appear to yield a new particle of mass 3, differing from the "H_3" of positive-ray methods of gas analysis in that it carries two units instead of one of positive electricity, and therefore is presumably an isotope of helium.

Nitrogen, however, differed sharply from oxygen in giving, in addition to these new particles, a very much smaller number (about one-twelfth) of H-particles. The range of these is slightly greater than of those obtained from hydrogen, but their identity was proved by direct comparison of the electromagnetic deviation in the apparatus above referred to.[8] It is estimated that, to produce 1 cubic millimetre of hydrogen by this means, the total α-radiation of 2 kilograms of radium acting for a year would be required.

So far as can be seen, artificial disintegrations of atoms by collision with the α-particle appear to be endothermic. The particle of mass 3 appears to escape with rather more than the energy of the α-particle striking the nucleus of the oxygen or nitrogen atom. Even neglecting the kinetic energy of the residue of the nucleus and of the α-particle after the collision, the dis-

[6] (Sir) E. Rutherford, *Phil. Mag.*, 1919, [vi], **37**,·571 ; *A.*, 1919, ii, 259.

[7] *Ibid.*, Bakerian Lecture, *Proc. Roy. Soc.*, 1920, [A], **97**, 374 ; *A.*, ii, 541.

[8] *Ibid.*, *loc. cit.*, and *Phil. Mag.*, 1919, [vi], **37**, 581; *A.*, 1919, ii, 260.

integration, as in the case of the radio-elements themselves, must be accompanied by the liberation of energy. On the view that the actual energy required to bring about the disintegration is small, and that the energy of the α-particle is mainly expended against the strong repulsive field, in getting near enough to the nucleus to affect it, electrons or β-rays, which would move up to the nucleus in an attracting field, may be able to bring about similar changes. This raises anew the whole question, so frequently discussed in these Reports,[9] as to the origin of the helium, found by some and not by other investigators, after passage of the electric discharge through gases in vacuum tubes and in old X-ray bulbs and the like. The latest experimental contribution gave negative results, in so far as the discharge through carefully purified hydrogen is concerned. In no case was helium or neon detected.[10] Naturally, these highly significant results have produced a flood of speculation as to the constitution of the atomic nucleus, which does not yet call for consideration here.

Isotopes.

Our knowledge of the heterogeneity of common elements has been notably advanced, during the period under review, beyond that recorded in the Reports four and seven years ago,[11] by the perfection of the positive-ray method of gas analysis and its application to the detection of heterogeneity, if it exists, in some nineteen non-radioactive elements.[12] The methods depend on the same general principles as those which sufficed to detect the presence of meta-neon, of atomic mass 22, in atmospheric neon in 1913, but the electromagnetic and electrostatic deviating fields are rearranged in such a way as to secure an effect precisely analogous to focussing in optics. The trajectories of the positive ions in a slightly divergent beam are brought to a focus in a plane containing the photographic plate. All those for which the value of the mass divided by the charge is the same are brought to the same point in the plane, those with greater and less values, respectively, being on either side. The complex pencil is resolved into a "mass spectrum" in every respect analogous to a light spectrum produced by a prism or grating. The terms "first-order and second-

[9] *Ann. Reports,* 1914, **11**, 45, 289.

[10] A. Piutti and E. Cardoso, *Gazzetta,* 1920, **50**, i, 5 ; *A.,* ii, 311.

[11] *Ann. Reports,* 1916, **13**, 245 ; 1913, **10**, 265.

[12] F. W. Aston, *Nature,* 1919, **104**, 334, 393 ; 1920, **105**, 8, 547 ; **106**, 468 ; *Phil. Mag.,* 1919, [vi], **39**, 449, 611 ; **40**, 628 ; *A.,* ii, 277, 344, 718.

"order mass-spectrum" are used to denote spectra produced by ions singly and doubly charged respectively. The existence of ions with more than one unit of charge introduces a complication, but fortunately these are experimental peculiarities which enable the two orders usually to be distinguished without uncertainty. The relative mass of the ion causing any line in the spectrum can so be evaluated to an accuracy of one part in a thousand, and the atomic mass determined to a degree of accuracy comparable with that attained in the best determinations of the atomic weight by chemical means. Incidentally, the complete agreement between the two in many cases affords much the most important evidence of the constancy between mass and weight for different elements. This question has been much canvassed of recent years.

Of the nineteen elements so far examined, ten prove to be homogeneous and nine to be heterogeneous and composed of more than one isotope with different atomic masses. The following table, taken from the author's last communication to *Nature*, gives the results.

TABLE OF ELEMENTS AND ISOTOPES.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes, in order of their intensity.
Hydrogen	1	1·008	1	1·008
Helium	2	3·99	1	4
Boron	5	10·90	2	11, 10
Carbon	6	12·00	1	12
Nitrogen	7	14·01	1	14
Oxygen	8	16·00	1	16
Fluorine	9	19·00	1	19
Neon	10	20·20	2	20, 22, (21)
Silicon	14	28·30	2	28, 29, (30)
Phosphorus	15	31·04	1	31
Sulphur	16	32·06	1	32
Chlorine	17	35·46	2	35, 37, (39)
Argon	18	39·88	2	40, 36
Arsenic	33	74·96	1	75
Bromine	35	79·92	2	79, 81
Krypton	36	82·92	6	84, 86, 82, 83, 80, 78
Iodine	53	126·92	1	127
Xenon	54	130·32	5 (7)	129, 132, 131, 134, 136, (128, 130 ?)
Mercury	80	200·60	(6)	(197–200), 202, 204

(Numbers in brackets are provisional only.)

Apart from a possible uncertainty, already alluded to, as to the order of spectrum to which any line belongs, the photographs published reveal the great power and certainty of the new method. Unfortunately, only non-metallic elements have so far been included. The difficulties in the way of examining metallic elements by this means have not yet been overcome.

In every case, except hydrogen, the atomic mass of each homogeneous component proves to be an exact integer, in terms of that of oxygen as 16, within the error of measurement already stated. For hydrogen, however, the chemical value, 1·008, is exactly confirmed and its homogeneity proved. Hydrogen, of course, is an exception to every generalisation concerning the chemical elements, and its simple structure, consisting probably of a single positive charge as nucleus and a single electron as satellite, is a sufficient reason for its uniqueness. If the hydrogen nucleus is the elementary positive constituent of the nuclei of other atoms, a number of electrons, equal to the difference between the atomic weight and atomic number, must be present also. Thus, if the nucleus of uranium is made up of 238 hydrogen nuclei, there must be in the nucleus $238-92=146$ electrons. The close packing of these positive and negative constituents may account for the difference of mass, 1·9 units, between the mass of the constituents and that of the resulting atom, that is, essentially to the difference in the atomic weights on the basis $H=1$ and $O=16$.[13]

The integral value of the atomic weights then points to an atomic constitution of secondary units, such as helium nuclei, packed sufficiently openly not to influence their mutual masses, the whole of the packing effect being due to the close packing within these secondary units.

Isotopes of Lead.

Atomic Weight of Lead of Radioactive Origin.—Fuller details of the atomic weight determination of the lead from Norwegian thorite, which gave 207·9, the highest yet found, have been published, together with those found for lead from three Ceylon thorianites, particulars of which follow:[14]

	Per cent. Th.	Per cent. U.	Per cent. Pb.	At. wt.
I.	68·9	11·8	2·3	207·21
II.	62·7	20·2	3·1	206·90
III.	57·0	26·8	3·5	206·83

Lead separated from samarskite, containing 12·2 per cent. of U_3O_8 and 1·03 per cent. of ThO_2, gave the value 206·30.[15] Lead from a Japanese source, of possible, though doubtful, radioactive origin, gave the value 207·13, which does not differ appreciably from that of common lead.[16]

[13] Compare *Ann. Reports*, 1916, **13**, 253.
[14] Compare *Ann. Reports*, 1918, **15**, 201; O. Hönigschmid, *Zeitsch. Elektrochem.*, 1919, **25**, 91; *A.*, 1919, ii, 285.
[15] A. L. Davis, *J. Physical Chem.*, 1918, **22**, 631; *A.*, 1919, ii, 107.
[16] T. W. Richards and J. Sameshima, *J. Amer. Chem. Soc.*, 1920, **42**, 928; *A.*, ii, 434.

Melting Point.—Two determinations show that, within the error of measurement, the melting point of lead of radioactive origin is identical with that of common lead. In one,[17] the lead, compared with common lead, had the atomic weight 206·57. A constantin-manganin couple was used, and the melting points were found to be identical to 0·5°, the experimental error. In the other,[18] thermocouples of copper–nickel were employed, the single couple being capable of reading hundredths, and the multiple couple thousandths, of a degree.

The lead compared in this case was from an Australian radio-active mineral of atomic weight 206·6. Neither specimen was spectroscopically pure, the common lead being the less pure, but probably the impurities did not exceed 0·005 per cent. They showed slight differences of behaviour. The super-cooling was greater for the purer sample, and its freezing-point–time curve was more horizontal. The radioactive lead had the higher melting point by 0·05°, but part, if not all, of this difference is to be ascribed to its greater purity. The thermo-electric power, electric conductivity, and change of the latter with temperature and pressure, were for each sample the same. These negative results thus have now decided between opposing theoretical views before discussed.[19]

Spectrum.—The minute difference, 0·0043 Å., in the wave-length of the line 4058 Å., already reported, has been confirmed.[20] Ordinary lead, lead from Joachimsthal pitchblende of undeter-mined atomic weight, and lead from Ceylon thorite of atomic weight 207·77, were compared. The method consisted in photographing the respective interference fringes, produced by a Fabry and Perot *étalon*, the source of light being an arc between an alloy of cadmium with the lead and a button of tungsten in a vacuum. Important sources of error present in the first series of experi-ments,[21] which gave a negative result, were eliminated by reducing all observations to a selected cadmium fringe as standard, which registers any variation due to a change of temperature or to the wandering of the source of light. These causes affect the standard fringe equally with the fringe under examination, and are so eliminated. The wave-length for the pitchblende lead was found to be 0·0050 Å. ±0·0007 Å. greater than that for ordinary lead,

[17] M. Lembert, *Zeitsch. Elektrochem.*, 1920, **26**, 59; *A.*, ii, 216.

[18] T. W. Richards and N. F. Hall, *J. Amer. Chem. Soc.*, 1920, **42**, 1550; *A.*, ii, 622.

[19] *Ann. Reports*, 1916, **13**, 252.

[20] Compare *Ann. Reports*, 1918, **15**, 204; T. R. Merton, *Proc. Roy. Soc.*, 1920, [A], **96**, 388; *A.*, ii, 140.   [21] *Ann. Reports*, 1916, **13**, 248.

which, in turn, was 0·0022 Å.±0·0008 Å. greater than that for thorite lead. Also, a difference was found for the wave-length of the line 5350 Å. of thallium when ordinary thallium and the thallium contained in pitchblende residues were compared, the former being the greater by 0·0055 Å.±0·001 Å. In this case, owing to the thallium not having been separated from the residues, ·the result cannot be entirely depended on, for the displacement of lines, by the presence of impurities, in the arc spectrum, though rare, is not entirely unknown. But it indicates a presumption that the thallium in pitchblende is of radioactive origin and different in atomic weight from ordinary thallium.

In an interesting discussion of the spectra of isotopes,[22] it is pointed out that the differences in the case of lead, although only of the order of a millionth of the wave-length, are one hundred times greater than are to be expected from the Bohr theory, as corrected to take into account the displacement of the centre of mass of the vibrating system with a change of the mass of the nucleus. They are enormously greater than can be ascribed to any purely gravitational effect of the mass of the nucleus on the electron. The result indicates the existence of a force, due to the mass of the nucleus, on the electronic system of the atom not hitherto known. In the original experiments, in which a 25 cm. grating was used and the spectrum photographed in the sixth order, the line was shifted, not broadened, to a position corresponding with the mean atomic weight of the lead, although a broadening, if not an actual resolution, into two or more lines corresponding with the separate isotopes present, in these circumstances, although not in the subsequent *étalon* experiments, is apparently to be expected. This minute difference of wave-length of the lines in the spectrum is the only difference in the physico-chemical properties of isotopes, apart from atomic mass, so far substantiated.

Separation and Properties of Isotopes

It cannot yet be considered proved beyond doubt that any actual analytical separation of the components of a mixture of isotopes has been effected. Systematic fractionation of atmospheric neon by the use of cold charcoal failed to effect any separation. Even fractional diffusion through pipe-clay has not, so far, given consistently positive results.[23] The theoretical question of the possi-

[22] W. D. Harkins and L. Aronberg, *J. Amer. Chem. Soc.*, 1920, **42**, 1328 ; *A.*, ii, 541.

[23] F. A. Lindemann and F. W. Aston, *Phil. Mag.*, 1919, [vi], **37**, 523 ; *A.*, 1919, ii, 209.

bility of separation by various means has been much discussed.[24] Methods, such as fractional diffusion, centrifugal separation, and thermal diffusion, which depend on differences of molecular mass, if not those, such as vaporisation and chemical fractionation, ought theoretically to be effective. The thermal diffusion method, depending on the maintenance of two intercommunicating vessels at widely different temperatures, which produces a condition of equilibrium, in which excess of the heavier constituent is present in the colder vessel, and centrifuging, both appear promising from the theoretical point of view.

Preliminary announcements of the partial separation of the isotopes of chlorine, mercury, and iodine (!) have been made. In the first case,[25] indications of a separation of hydrogen chloride by fractional diffusion into a heavier and lighter fraction have been announced, but no definite experimental data are given. In the case of mercury,[26] evaporation at low pressure is stated to give a condensate less in density than the residual mercury. Each fraction was redistilled before the density was taken, and the difference in the pyknometer determinations amounted to 5 parts in 100,000, the error of measurement being less than one part in a million. Iodine, the most recent of the elements to be submitted to positive ray analysis, and found, unlike chlorine and bromine, to be homogeneous, has, from speculative reasoning, been ascribed five isotopes. Fractional diffusion gave products with atomic weight varying from 128·22 upward, the mean being 2·04 per cent. above the accepted value.[27]

Very interesting new results have been obtained along the lines of the use of radioactive isotopes of common metals to indicate what is occurring to the latter in chemical operations. Thus it has been shown that a free exchange of the metallic atom among the competing acid radicles occurs for ionised, but not for non-ionised, compounds. The general method was to mix solutions of two different compounds of lead in equimolecular proportions, the one compound only being "activated" by presence of thorium-*B*, which is isotopic with lead, and to determine the activity of the lead in the less soluble compound crystallising out. When active lead nitrate and inactive lead chloride are dissolved in molecular

[24] F. A. Lindemann, *Phil. Mag.*, 1919, [vi], **38**, 173 ; S. Chapman, *ibid.*, 182 ; *A.*, 1919, ii, 390.

[25] W. D. Harkins, *Nature*, 1920, **105**, 230 ; *Science*, 1920, **51**, 289.

[26] J. N. Brönsted and G. von Hevesy, *Nature*, 1920, **106**, 144.

[27] E. Kohlweiler, *Zeitsch. physikal. Chem.*, 1920, **94**, 513 ; **95**, 95 ; *A.*, ii, 610, 615.

proportion in boiling pyridine, the lead in the lead chloride crystallising out is half as active as the lead in the original lead nitrate, but when an active lead salt is so mixed with an organic compound of lead, such as lead tetraphenyl or diphenyl nitrate, in suitable solvents, no interchange of lead occurs, and the active lead salt retains its original activity. This constitutes something· like a direct proof of the ionic dissociation theory and of the current views as to the difference between the nature of chemical union in electrolytes and non-electrolytes. When the acetates of quadrivalent activated lead and of bivalent inactive lead are mixed in glacial acetic acid, the activity of the first compound, after crystallising out from the mixture, is reduced to one-half. This indicates, since the two lead ions differ only by two electrons, a free interchange of electrons between them and a dynamic equilibrium between ions and electrons, and between free electrons and the electrodes in electrolysis.[28]

Isotopes have been ·used to determine the velocity of diffusion of molecules among themselves. The rate of diffusion is dependent on the molecular diameter, and not on the mass, so that a radioactive isotope diffusing among the inactive molecules of the same type of element affords the means for investigating experimentally ·this otherwise insoluble problem. The case has been tried with molten lead. At the bottom of a narrow, vertical tube was placed a layer of lead rendered active by the presence of thorium-B, and above it a layer three times the height of common lead. The whole was kept at 340° for several days. After cooling, the cylinder was cut up into four equal lengths, each melted and hammered into foil, and the concentration of thorium-B in each determined by a-ray measurements. Values for the diffusion coefficient between 1·77 and 2·54 per sq. cm. per day, with a mean of 2·22 in seventeen experiments, were obtained. This corresponds with a diameter of the lead molecule between 0·78 and 1·16($\times 10^{-8}$ cm.), according to the formulæ used to connect the two quantities. The value found, when reduced to a temperature of 18° and for a fluid of the viscosity of water, becomes 2·13. Since the value for lead ions diffusing in aqueous solutions is 0·68, this indicates that the molecular diameter in the case of metallic lead is only a third of that in the case of the ion, and shows that the latter is probably hydrated.[29]

[28] G. von Hevesy and L. Zechmeister, *Ber.*, 1920, **53**, [B], 410 ; *A.*, ii, 278 ; *Zeitsch. Elektrochem.*, 1920, **26**, 151 ; *A.*, ii, 345.

[29] J. Gróh and G. von Hevesy, *Ann. Physik*, 1920, [iv], **63**, 85 ; *A.*, ii, 739.

Researches analogous to those reported have led to the detection and isolation of volatile hydrides of lead and tin.[30]

The " Fixed Electron " Type of Atomic Structure.

A notable rival has been developed to the view described in the last Report [31] of an atom in which the electrons are supposed to revolve in orbits around the nucleus, with special assumptions as regards the radiation of energy in quanta rather than continuously. In this atom, the electrons surrounding the nucleus are supposed to occupy, or oscillate about, certain fixed positions in the structure. This fixed electron type of atom has been found to possess many advantages in chemistry and physics, notably in accounting for the Periodic Law, the various categories of chemical compounds, ionised and un-ionised, and the arrangement of the atoms in the crystal space-lattice as determined by X-ray methods. It may be said to draw its underlying postulates from facts in these fields rather than from any purely mathematical or fundamental reasoning.[32] The chief idea is that, in the outermost shell of electrons surrounding the nucleus, the electrons tend to form an octet and to occupy the corners of a cube. In the outermost shell all eight corners are occupied in those atomic structures corresponding with the zero family of chemically inert gases. The chemical activity of other elements is due to some of the corners being not occupied by electrons, whereby two or more atoms tend chemically to "combine." The combination may be of two kinds. Either the atoms with only a few of the corners occupied by electrons, that is, of those elements in the first families of the Periodic Table, lose their electrons altogether, forming positive ions, such as Na‘, Mg‘‘, Al‘‘‘, to the atoms which have all but a few of the corners occupied, that is, of those elements in the last families of the Periodic Table, with the formation of the negative ions, such as Cl′, S″, or more often to groups of these atoms. This way of regarding ionised compounds was, of course, arrived at long before this theory was proposed, but it emphasises the completely separated existence of the two ions forming the molecule, even in the solid state, which is supported by the character of the space lattices of the crystals

[30] *Ann. Reports*, 1918, **15**, 225 ; 1916, **13**, 266 ; F. Paneth and K. Fürth, *Ber.*, 1919, **52**, [B], 2020 ; F. Paneth and O. Nörring, *ibid.*, 1920, **53**, [B], 1693 ; *A.*, ii, 41, 758.

[31] *Ann. Reports*, 1918, **15**, 206.

[32] G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762 ; *A.*, 1916, ii, 310 ; I. Langmuir, *Proc. Nat. Acad. Sci.*, 1919, **5**, 252 ; *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543 ; 1920, **42**, 274 ; *A.*, 1919, ii, 328, 506 ; 1920, ii, 243 ; *Science*, 1920, **51**, 605 ; *A.*, ii, 656 ; W. Kossel, *Zeitsch. Physik*, 1920, **1**, 395 ; *A.*, ii, 681.

of salts. The forces at work are the opposed charges on the ions which act statistically, n sodium ions requiring the simultaneous presence of n chlorine ions, rather than each sodium atom being attached to one chlorine atom, as in the formula Na–Cl.

In the second kind of combination, namely, that corresponding with definite atomic linkings, such as are regarded to exist between the atoms of the molecule in organic compounds and in non-electrolytes generally, the theory is more original. Different atoms so rigidly linked together are regarded as sharing electrons in pairs. Two electrons held in common by two atoms constitute the ordinary single bond. The cubes are attached edge to edge. Four electrons in common correspond with a double bond. The cubes are attached face to face. A corner to corner attachment of two cubes, which the single bond most closely suggests, is not considered to occur at all. The sharing of a pair of electrons by two atoms is regarded as the single unit of valency.

In addition to this type of definite linkage, two others are postulated. The hydrogen nucleus is capable of sharing a pair of electrons, its own and one derived from another atom, either an atom of itself, as in the hydrogen molecule, or an atom containing an uncompleted octet. Thus in water the oxygen nucleus is at the centre of a cube of electrons, two pairs of which, at two opposite pairs of contiguous corners, being shared with two external hydrogen nuclei. Pairs so held are supposed to be drawn closer together, distorting the cube. In this way, the tetrahedral character of the carbon atom is accounted for. The uncombined atom of carbon, if it existed free, which, of course, never occurs, would have four of the eight corners of the cube occupied with electrons. If symmetrically distributed, these would occupy the corners of a regular tetrahedron. When it shares these in pairs with electrons of other radicles or atoms in compounds, the drawing together of each pair shared preserves the tetrahedral character of the arrangement in the combined atom. The facts of stereochemistry require free rotation to be possible about a single bond, and not about a double bond, whereas, unless further assumptions are made, such as that the pair are drawn together to one point or supposed to rotate round one another, free rotation would not be a possibility for a single linkage on this theory. The existence of triple bonds again, which is possible on a tetrahedral, is impossible on a cubic atom, if only partly deformed to a tetrahedron.

The second type of combination postulated is rather surprising in that a pair of nuclei are supposed to be contained in a single cube, or octet, in such combinations as the nitrogen molecule,

carbon monoxide, hydrocyanic acid, and nitric oxide. If this is correct, such compounds would represent, as it were, structures half-way between those typical of atoms and molecules respectively. Although something might be said for such a structure representing the properties of nitrogen, one would scarcely have expected it to be capable of representing also such an extremely active gas as nitric oxide.

Into this theory of valency, which so far seems to be confined mainly to the lighter elements in the earlier part of the Periodic Table, it is unnecessary further to enter here. Of more topical significance is the way in which the atomic numbers of the Periodic Law are accounted for. The atom is regarded as made up of concentric shells of electrons of relative diameter 1, 2, 3, 4, and relative area 1, 4, 9, 16. Each electron is regarded as occupying the same superficial area, to whatever shell it belongs. The inert gases are the elements for which the outer shell contains its full complement of electrons. Helium, of atomic number 2, has two electrons at the poles of the first shell. The line joining them and passing through the nucleus is regarded as the polar axis of the atom. The plane passing through the equator divides the shell into two hemispheres. There are no electrons in the equatorial plane of any atom. In the outer shells, concentric with the first, they are distributed according to the symmetry of a tetragonal crystal. Four secondary planes of symmetry, at 45° with each other, pass through the polar axis. The second completed shell, being four times the area of the first, contains eight electrons, occupying the eight corners of a cube. This is the neon atom. The atomic number is 10, and it contains eight electrons in the second shell—four in each hemisphere above and below the equatorial plane—and two in the first. or helium, shell. Every shell, other than the innermost, after getting filled up with electrons once, is filled up twice, and the next inert gas is argon, atomic number 18, containing sixteen electrons in its second shell and two electrons in its first. In the next, krypton, of atomic number 36, the third shell contains eighteen electrons, two distributed at the poles and the other sixteen symmetrically with regard to the polar axis and the sixteen underlying electrons of the second shell. By filling the third shell again we get xenon, of atomic number 54. The fourth shell contains thirty-two electrons, and the next inert gas must have an atomic number 86. This is the correct atomic number for the emanations of the radioactive elements. Unfortunately, the Periodic Table comes to an end before this ingenious theory can be further tested. That, however, the table should proceed to uranium, which possesses complete chemical analogy to tungsten

and molybdenum, instead of to a second lot of rare earth elements, after radium and thorium, raises the doubt whether it just does not come to an end in time for the theory. Undoubtedly, however, it is an achievement, even by such arbitrary assumptions, to have accounted for the actual sequence of elements in the table at all.

The theory has found general support in the explanation of the arrangements of atoms in crystals as elucidated by X-ray methods.[33] It is possible to assign to each atom in the space-lattice a definite approximate diameter, and to regard the crystal as built of spheres of these diameters closely packed. When the atomic volumes corresponding with these diameters are plotted against atomic weights, a curve, in every respect analogous to Lothar Meyer's atomic volume curve, is obtained, but applicable to the compounds of the elements. Then it is found that two electro-negative elements are situated close together, and are assigned small diameters when, according to the above theory, they share electrons; but the electropositive elements, which exist as separated ions and do not share electrons with their neighbours, are situated at a distance from them, and appear to have large diameters. From crystal data, the diameter of the electronic shells corresponding with neon, argon, krypton, and xenon are put at 1·30, 2·05, 2·35, and 2·70 Ångström units respectively. The theory, being definite and easily visualised, if arbitrary, will doubtless justify itself in drawing attention to the many different types of chemical interaction, which hitherto have been too liable to be confused together and forced into a mould to fit just the one type of interaction which the ordinary valency-bond theory suffices to explain. It is not yet possible to bridge the gap between this idea and that of the rotating electron atom, which has grown up largely from the study of the wave-lengths of the characteristic X-rays themselves. Undoubtedly each type has its advantages, but for chemistry the fixed electron type seems easily to hold the field.

In the light of these advances, an experiment showing that the α-radiation from different faces of a large crystal of uranium nitrate was, within the error of experiment, of the same intensity. seems to show that the α-particles are shot out from the nucleus during disintegration. without relation to the orientation of the atomic axis, for it may be regarded as at least highly probable that in the crystal space-lattice the atoms have their axes orientated in a regular manner.[34]

[33] W. L. Bragg, Royal Institution Evening Lecture, May 28th, 1920 ; *Phil. Mag.*, 1920, [vi], **40**, 169 ; *A.*, ii, 537.
[34] T. R. Merton, *Phil. Mag.*, 1919, [vi], **28**, 463 ; *A.*. 1919, ii, 453.

High-frequency Spectra of the Elements.[35]

Work in this field proceeds apace, though without breaking much fresh ground. Precision measurements, to a degree of accuracy one-hundredfold greater than previously, have been carried out for the lines in the K series of a number of elements from chlorine to copper, and the results compared with the various mathematical formulæ proposed. The spectrum of tungsten, for which the K, L, and M series can all be studied, has also been examined, and a spectrograph constructed to bridge the gap between these two series of precision measurements.[36] The M series has been further investigated, and extended from uranium as far as dysprosium.[37]

New measurements of the absorption bands of thulium, neoytterbium, and lutecium in the K series have been made.[38]

An examination of the L absorption spectrum of a pure radium chloride solution gave two lines, 0·802 and 0·670 Å., in agreement with the atomic number 88 assigned by the Periodic Table.[39] By the use of a reinforcing screen of calcium tungstate, the β_1 line of the K spectrum of tungsten (0·1844 Å.) has been shown to be a doublet separated by about 0·0007 Å.[40] In an examination of the X-ray absorption spectrum of phosphorus, differences of wave-length were observed for different forms. The wave-length 5·767 Å. was found for the black phosphorus of Bridgeman, and 5·750 Å. for phosphoric acid and its ammonium salt, whilst red phosphorus shows. a double limit, corresponding with each of the two wave-lengths given. This is believed to be the first case noticed of the chemical state of an element affecting its X-ray spectrum.[41]

Arrangements have been described for the examination of the space-lattices of powdered materials, by which it has been shown that thorium and nickel in powder form have face-centred cubical lattices, and magnesium a lattice composed of two interpenetrating simple hexagonal lattices.[42]

X-Rays have also been used to determine the size and structure of the particles of organic and inorganic colloids. Gold and silver

[35] Compare *Ann. Reports*, 1916, **13**, 257.

[36] M. Siegbahn, *Phil. Mag.*, 1919, [vi], **37**, 601 ; **38**, 639 (and with A. B. Leide), 647 ; *A.*, 1919, ii, 261, 488, 489 ; E. Hjalmar, *Zeitsch. Physik*, 1920, **1**, 439 ; *A.*, ii, 655.

[37] W. Stenström, *Ann. Physik*, 1918, [iv], **57**, 347 ; *A.*, 1919, ii, 90.

[38] M. de Broglie, *Compt. rend.*, 1920, **170**, 725 ; *A.*, ii, 277.

[39] *Ibid.*, 1919, **168**, 854 ; **169**, 134 ; *A.*, 1919, ii, 207, 358.

[40] *Ibid.*, 1920, **170**, 1053 ; *A.*, ii, 344.

[41] J. Bergengren, *ibid.*, 1920, **171**, 624 ; *A.*, ii, 654.

[42] H. Bohlin, *Ann. Physik*, 1920, [iv], **61**, 421 ; *A.*, ii, 214 ; compare A. W. Hull, *J. Amer. Chem. Soc.*, 1919, **41**, 1168 ; *A.*, 1919, ii, 470.

in the colloid form possess the same space-lattices as in large crystals, even when the particles are too small to be visible under the ultramicroscope.   In old silicic acid and stannic acid gels, traces of crystalline structure can be detected, but not in the typical organic colloids, such as albumin, gelatin, cellulose, starch, and the like.[43]

It has been pointed out that it is a necessary consequence of the modern views of crystal structure that, in certain cases, the chemical composition of the crystal must depend on its size.   Thus iron pyrites, with a space-lattice consisting of an atom of sulphur within a cube, four alternate corners of which are occupied by iron atoms, instead of the formula FeS_2, must possess a composition given by $Fe_{(n+1)^3}S_{2n^3}$, where n is the number of elementary cubes in the crystal.   If n is 50, the particle would still be visible by the aid of the ultramicroscope, and its composition would be given by $FeS_{1\cdot885}$.[44]

α-Rays.

The   Geiger-Nuttall   Relation.—The   logarithmic   connexion between the period of average life of an atom and the range of the α-ray expelled from it during disintegration, and the theory of the cause of atomic disintegration to which it has led, have been the subject of closer examination.   On this theory,[45] the instability of the atom is supposed to result from the simultaneous conjunction of a large number, N, of separate particles, moving independently of one another within the atomic nucleus, in a certain favourable relation.   The chance of disintegration depends on something like the one-hundred-and-sixtieth power of the velocity of the α-particle expelled, and such a law can scarcely be explained except as an expression of the probability of the fortuitous occurrence of a very large number of independent events.

The actual value first deduced from the periods and ranges for N was about 80, a number of the same order as the atomic number. The relation between range and period on this theory becomes

$$\log \lambda = Na + \tfrac{2}{3}N \log R,$$

where R is the range and a is, approximately at least, a constant.

From new data on the ranges of some of the members of the various disintegration series, values for N, 81, 77, and 71, have been assigned for the uranium–radium, thorium, and actinium series respectively.[46]   Clearly these must be of the nature of mean

[43] P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96 ; *A.*, 1919, ii, 274.
[44] A. Quartaroli, *Gazzetta*, 1920, **50**, ii, 60 ; *A.*, ii, 609.
[45] *Ann. Reports*, 1916, **13**, 257.
[46] S. Meyer, V. F. Hess, and F. Paneth, *Sitzungsber. Akad. Wiss. Wien*, 1914, **123**, 2a, 1459 ; S. Meyer, *ibid.*, 1916, **125**, 2a, 201.

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values, since the number of independently moving particles in the nucleus must diminish by unity with each α- or β-particle expelled, that is, with each step in the disintegration series. The experimental numbers given for the uranium–radium and the thorium series agree with the mean values to be expected if the atomic nuclei are practically composed of helium nuclei and binding electrons. Thus for thorium, with atomic weight 232 and atomic number 90, 58 helium nuclei and $116 - 90 = 26$ binding electrons would constitute a system consisting of eighty-four independent units. The value of N for thorium itself would be one less, since the probability relation holds between one of the particles and the rest of the nucleus. The mean value for the series between thorium and thorium-C, considering N to be reduced by unity for each α- and for each β-particle expelled, would be 78 instead of the value found, 77. For the uranium atom, with atomic weight 238 and atomic number 92, two hydrogen nuclei at least must be postulated. If there are only two, there must be 59 helium nuclei and $118 + 2 - 92 = 28$ binding electrons, making a total of 89 independent particles. The mean of the number, diminished by one, is, for the series uranium to polonium, 81 or 82, again in excellent agreement with the experimental value.

If, now, the correct values for N are introduced for each member of the series, and the value of the constant a calculated, it is found that a is truly constant for the middle members of each series, but is markedly, although not greatly, different for the first and last members of each series [47] The actinium series is scarcely yet worth consideration here, as, in absence of all experimental evidence as to the atomic weights of its members, the values to be assigned to N must be a matter for speculation. In addition, it obeys the logarithmic relation only very imperfectly. The difficult question as to the cause of the disintegration of the atom in radioactive changes seems at least to be progressing towards a satisfactory and highly suggestive answer.

In other papers, Bohr's principle of angular momentum has been applied to the internal economy of the nucleus, and the conclusion reached that the motions of the particles remaining in the nucleus are not affected by the successive steps in the atomic disintegration. The radius of the orbit of revolution of the α-particle in the nucleus before expulsion has been calculated, and found to diminish by steps with each successive disintegration.[48]

A collection of papers has appeared on the counting and photo-

[47] G. Kirsch, *Physikal. Zeitsch.*, 1920, **21**, 452 ; *A.*, ii, 577.
[48] H. T. Wolff, *ibid.*, 175, 393 ; *A.*, ii, 366, 578.

graphic registration of α-particles. The electrometer method, using high potential gradients just below the sparking potential, whereby the ionisation is enormously magnified by collision, has been the one employed. As the most suitable gas for filling the counting chamber, a mixture of 54 per cent. of carbon dioxide and 46 per cent. of air was used. It was found that a mixture of carbon dioxide and air, with the former in excess, responded only to the α-rays, and not to the β- and γ-rays.

A new determination of the number of α-particles expelled per second per gram of radium (element), free from disintegration products, gave $3·72(±0·02) × 10^{10}$. In arriving at this value, 80,000 α-particles were counted. This is about 4 per cent. above the previously accepted value, even after correction in terms of the International Standard.[49]

In a special research, it was found that 1·5 milligrams per sq. cm. of mica, of density 2·87, correspond, in stopping power towards α-rays, with 1 cm. of air at 760 mm. and 15°.[50]

The individual intervals between the emission of α-particles by polonium have been systematically studied by photographic registration methods for the case of 10,000 emissions. The requirement of the theory of probability was very exactly verified. The fraction of the total number of intervals of duration greater than τ is $\epsilon^{-\theta/\tau}$, where θ is the mean interval. For very short intervals the law is departed from, owing to the emission of α-particles with intervals between them too small to be distinguished by the means employed. From the results obtained, the number of such "doublets" could be very exactly evaluated.[51]

An effect, analogous to the "spluttering" of metals under the action of the cathode rays in discharge tubes, has been observed with α-rays for the noble metals nickel and aluminium, but not for such metals as copper, the surface of which is easily oxidised by the action of the atmosphere. Another effect due to α-rays was observed with polonium, electrolytically deposited on metal foil. The α-particles emitted at grazing incidence appear to "knock off" the polonium in aggregates of several molecules at a time, causing an effect analogous to the volatilisation of the polonium, which is called "aggregate recoil." The effect is very much more pronounced in a vacuum than in the atmosphere. It is greatest with freshly deposited preparations, and diminishes with their age.

[49] *Ann. Reports*, 1914, **11**, 274.
[50] R. W. Lawson and V. F. Hess, *Sitzungsber. Akad. Wiss. Wien*, 1918, **127**, 2a, 405, 461, 535, 599, 943.
[51] (Mme) M. Curie, *J. Phys. Radium*, 1920, [vi], **1**, 12 ; *A.*, ii, 727.

The most regular results are obtained with palladium and platinum foils electrolytically saturated with oxygen. Saturating with hydrogen diminishes the effects and makes them irregular.[52]

γ-Rays.

In a continuation of the researches fully described in the last Report,[52a] two types of secondary γ-rays, referred to as S_1 and S_2, have been found to be associated with the two primary components of the γ-rays of radium, designated as K_1 and K_2. The first is of the nature of a scattered primary, possessing the same coefficient of absorption as K_1, and distributed with decreasing intensity with increasing angle of scattering. None is detectable at an angle of 90° or beyond, or, in other words, this secondary radiation is confined to emergence. For this type, the scattering power of different atoms is proportional to their atomic number. The type S_2 is, in general, different in penetrating power from K_2, and is scattered over an angle of 180°, constituting an incident, as well as emergent, radiation. For light atoms the scattering is proportional to the atomic number, but for heavy atoms to the square of this number.[53] The absorption of divergent beams of γ-rays has also been studied, with the view of throwing light on the reason why γ-rays, although complex and scattered, so nearly obey the theoretical law of absorption to be expected for a homogeneous, non-scattered beam.[54]

Methods have been developed for "counting" γ-rays analogous to those referred to under "α-Rays." The effect of a γ- or β-ray is, in general, twenty to twenty-five times less than that of an α-ray, but with a sufficiently sensitive counting arrangement they may be counted with ease and certainty. Some special precautions are taken, on account of the high potential necessary to render the response very sensitive, but otherwise the arrangements are very much as for the α-rays. The gas used in the counting chamber is air, drawn from the free atmosphere and stored over sulphuric acid until any emanation initially present has had time to decay, and filled into the chamber through cotton wool and phosphoric oxide.

The γ-ray acts by liberating a high-velocity β-particle from the metal walls of the counting chamber, and the same methods are

[52] R. W. Lawson, *Sitzungsber. Akad. Wiss. Wien,* 1918, **127,** 2a, 1315 ; 1919, **128,** 2a, 795.

[52a] *Ann. Reports,* 1918, **15,** 211.

[53] K. W. F. Kohlrausch, *Sitzungsber. Akad. Wiss. Wien,* 1919, **128,** 2a, 853.

[54] *Ann. Reports,* 1918, **15,** 213 ; M. Blau, *Sitzungsber. Akad. Wiss. Wien,* 1918, **127,** 2a, 1253.

equally applicable for β- as for γ-rays. It was found that the number of γ-rays given per atom from radium-*B* and radium-*C*, respectively, were practically the same. The total number of γ-rays from both together is, in terms of the number of α-particles from radium-*C*, between two and one.[55]

Chemical Actions of the Rays of Radium.

The reactions proceeding in common gases, when mixed with radium emanation, and due to α-rays, have been the subject of two exhaustive investigations, chiefly to ascertain whether the facts are in agreement with the theory that the reactions obey a form of Faraday's law, that the molecules formed in the reaction are equal in number to the pairs of ions formed from the rays in the gas.[56] In one research, four gases, hydrogen sulphide, ammonia, nitrous oxide, and carbon dioxide, were studied. Other conditions being the same, the amount of decomposition is proportional to the amount of emanation present. The decomposition increases as the size of the reaction vessel is increased, to a limit corresponding with the state in which practically the whole of the energy of the α-rays is spent in traversing the gas molecules. For hydrogen sulphide, the thermal coefficient of the velocity of reaction is practically zero from −180° to 18°, and above this, to 220°, is slightly negative. For nitrous oxide, the reaction proceeds probably in two directions, for the most part with the formation of nitrogen and oxygen, but also with the formation of nitric oxide and nitrogen. The accumulation of nitrogen peroxide as a result of the second reaction retards the reaction. Here, again, changes of temperature produce but a slight effect on the velocity of reaction, the coefficient being negative below and positive above 18°. For ammonia, the coefficient is positive and considerable up to 220°. Carbon dioxide was found to undergo only a very slight decomposition, and the rapid change recorded by other investigators is attributed to the effect of mercury and phosphorus in the vessel.

For these reactions, Faraday's law was found not to apply. The ratio between the number of molecules produced and the number of pairs of ions formed by the α-rays exceeds unity in cases where no catalytic action is involved.[57]

In the other research, the combination of hydrogen and oxygen was re-studied. Here it was found that 3·92 molecules of water result for every pair of ions formed in the gas. It appears that

[55] V. F. Hess and R. W. Lawson, *Sitzungsber. Akad. Wiss. Wien*, 1916, 125. 2a, 285, 585, 661.   [56] *Ann. Reports*, 1912, 9, 322.
[57] E. Wourtzel, *Le Radium*, 1919, 11, 289, 332; *A.*, ii, 214.

in all the earlier results of Ramsay and Cameron, which gave support to the ionisation theory, the amount of emanation used had been much overestimated. It had been calculated from the time of accumulation and quantity of radium, which, since the development of exact methods of measuring the emanation by the γ-rays, is known to be quite untrustworthy. The velocity of reaction was found to be proportional to the quantity of emanation and independent of the temperature. It was increased by increase of oxygen above the stoicheiometrical proportion, the velocity of reaction continuing to rise as this excess increases with the reaction, and diminished by increase of hydrogen, the velocity continuing to fall as the excess of hydrogen increases. This is to be expected from the ionisation theory, since the relative ionisations in oxygen and hydrogen are as 1·09 to 0·24, that of air being unity.

In very small vessels, particularly at low pressures, the velocity of reaction is abnormally high. This is ascribed to the atom of radium-A, recoiling from the atom of emanation, bringing about the combination in the same way as an α-particle. Under the most favourable conditions for magnifying this recoil effect relatively to that produced by the α-rays, it may exceed the latter six or seven times. The relative effect produced is in agreement with the data as to the magnitude of the ionisation produced by recoil atoms.

With the single exception of hydrogen and chlorine, where the chemical action may be several thousand times as great as the ionisation theory requires, it is claimed that there is a general statistical agreement between the number of ions and the number of molecules produced for a large number of reactions. The two numbers are not the same, but they correspond within a multiplier of a few units only in either direction. This is true for reactions produced by the cathode rays and β-rays, as well as those resulting from the action of α-rays and recoil atoms. The ratio of four to one, in the present case, between the numbers of the molecules and ions can be explained by ionic possibilities, without recourse to other theories.[58]

In the reverse reaction, the decomposition of liquid water by the α-particle into hydrogen and oxygen, about one molecule of water is decomposed per pair of ions formed. In practice, the recombination of hydrogen and oxygen under the action of the emanation proceeds almost to completion at constant volume, because the water condenses to droplets, and so is removed for the most part from the action of the α-rays.[59]

[58] S. C. Lind, *J. Amer. Chem. Soc.*, 1919, **41**, 531, 551 : *A.*, 1919, ii, 210.
[59] *Idem*, *Trans. Amer. Electrochem. Soc.*, 1918, **34**, 211.

The long series of parallel experiments on the action of the penetrating rays of radium and of ultra-violet radiation from a quartz mercury lamp on organic substances has been continued. The substances studied comprise a mixture of maleic and fumaric acids, solutions of formic and benzoic acids and of carbamide, dry and wet toluene, chloroform, and carbon tetrachloride. The effects of the two kinds of irradiation are, in general, similar, the ultra-violet light being usually almost incomparably the more rapid. The results bear out the general view that these agents have a shattering effect on almost all molecules, followed by numerous secondary reactions among the products.[60]

The thermoluminescence and decolorisation of glass which has been exposed to the rays of radium, on heating, have been shown to be independent of one another. For freshly exposed glass, thermoluminescence starts on heating below 100°, and at 200° for specimens exposed some years previously. Decolorisation does not, however, occur until the temperature of 500° is reached.[61] The colorations and thermoluminescence produced in a great variety of minerals have been examined. The fluorspars, by reason of the almost bewildering variety of colour changes they undergo and the brilliance of the thermoluminescence produced, are among the most interesting.[62] In this connexion, the variety of fluorspar from Wölsenberg, Bavaria, locally called "Stinkfluss," deserves special mention. On being crushed, it emits a peculiar odour, which those who have made a careful study of the mineral assert is without doubt due to free fluorine. Radium rays easily reproduce the natural dark blue colour in the mineral after the colour has been discharged by heating, but do not restore its odoriferous quality.[63]

Studies of Radioactive Minerals.

Age of Thorium Minerals.—In a careful review of the difficult questions connected with the age of thorium minerals, both the isotopes of lead derived from thorium are regarded as stable, and the age of the mineral, A, is deduced from the formula

$$A = \frac{Pb}{U + 0\cdot384\ Th} \times 7,900 \text{ million years,}$$

where Pb, U, and Th are the percentages of these elements in the

[60] A. Kailan, *Zeitsch. physikal. Chem.*, 1920, **95**, 215 ; *A.*, ii, 576 ; *Sitzungs-ber. Akad. Wiss. Wien*, 1919, **128**, 2a, 831 ; 1917, **126**, 2a, 741.

[61] S. C. Lind, *J. Physical Chem.*, 1920. **24**, 437 ; *A.*, ii, 576.

[62] E. Newbery and H. Lupton, *Mem. Manchester Phil. Soc*, 1918, **62**, No. 10 ; *A.*, 1919, ii, 130.

[63] F. Henrich, *Zeitsch. angew. Chem.*, 1920, **33**, 5, 13, 20 ; *A.*, ii, 216.

mineral. The conclusion is reached that in (1) the Middle-Devonian formation at Brevig, Norway, in the Precambrian formations of (2) Arendal-Gegend, Norway, and (3) Moss, Norway, and (4) in the thorianite-bearing pegmatites of Ceylon, all those minerals with less than three times as much thorium as uranium give quite concordant ages for the formations, namely, (1) 300, (2) 1300, (3) 950, (4) 500 million years, respectively. These must be regarded as true primary minerals; but all those for which the Th/U ratio is greater than 3 give smaller ages, and must be regarded as secondary minerals derived from the primary by various processes of change in which the content of thorium has been enriched. In the first class are to be found, in (1) eudidymite, eucolite, zircon, pyrochlor, and biotite, in (2) cleveite, in (3) broeggerite, and in (4) pitchblende and thorianite, whilst in the second class are, in (1) freyalith, thorite, and orangeite, in (2) uranothorite and orangeite, in (3) uranothorite of Hitterö, and in (4) thorite. The atomic weights of the lead from the three varieties of thorianite, already given, conform well to the view that they are primary constituents of the pegmatite, which has an age between 400 and 500 million years.[64]

The ratio of thorium to uranium in a number of minerals has been determined by radioactive methods. In Morogoro pitchblende there is 0·5 per cent. of thorium and 74·5 per cent. of uranium; in pitchblende of St. Joachimsthal, per gram of uranium, $4·68 \times 10^{-5}$ grams of thorium, making, with the estimated $1·96 \times 10^{-5}$ grams of ionium, a total $6·64 \times 10^{-5}$ grams of thorium isotopes. A monazite sand of unstated origin, containing 7·23 per cent. of thorium, was found to contain 0·087 per cent. of uranium.[65] In another estimation, monazite sand from Brazil was found to contain 0·8, and from India 0·102 ($\times 10^{-9}$ gram of radium per gram). These correspond with 0·235 and 0·03 per cent. of uranium respectively, and, on a thorium content of 4 and 9 per cent., mesothorium preparations obtained from them would owe 28 and 2·1 per cent., respectively, of their initial γ-activity to radium.[66]

In a monograph on broggerite, which contained 63—66 per cent. of uranium, 6—6·5 per cent. of thorium, 9·5—10 per cent. of lead, and 0·7—1·5 per cent. of rare earths, hydrofluoric acid

[64] R. W. Lawson, *Sitzungsber. Akad. Wiss. Wien*, 1917, **126**, 2a, 721; A., ii, 149.

[65] S. Meyer, *ibid.*, 1919, **128**, 2a, 897; A., ii, 548.

[66] J. E. Underwood and H. Schlundt, *Trans. Amer. Electrochem. Soc.*, 1918, **34**, 203; A., ii, 146. (In the abstract, 10^{-7} gram should read 10^{-9} gram.)

was found to be the best precipitant for thorium in presence of uranium. As is well known, the method of separation based on the solubility of uranium nitrate in ether or acetone is useless. The Pb/U ratio in this mineral is essentially constant at 0·12 to 0·13, which corresponds well with the age of about a thousand million years, already given, for the pegmatite dykes in the granites of Moss, Norway, from which it is obtained.[67]

The Uranium–Radium Ratio.—This important ratio has been redetermined for a carefully selected Colorado pitchblende. The uranium was estimated analytically, and the radium by the emanation method against specially made absolute standards of radium. These were prepared, by dilution to $1·5 \times 10^{-9}$ grams of radium per c.c., from a radium chloride of 100 per cent. purity, measured against the International Standard by γ-rays. A million times the quantity of barium was added to the diluted standard to protect the minute amount of radium from precipitation. The result gave $3·4 \times 10^{-7}$ grams of radium as the quantity in equilibrium with 1 gram of uranium. This was the original "Rutherford-Boltwood" value, but it was subsequently corrected to $3·23 \times 10^{-7}$ on the International Standard. Much independent work has shown that the uncorrected value was substantially correct, and it is very satisfactory to have had this conclusion confirmed so convincingly.[68]

Relative α-Activities of Uranium and Radium.—Many points remain to be cleared up with regard to the relative α-activities of radium and uranium minerals. A new determination has substantially confirmed the original determinations. Taking the activity contributed by uranium (U-*I* and U-*II*) as unity, the total activity of the mineral is now found to be 4·73 instead of 4·69, and the part due to radium itself as 0·488 in place of 0·45. If, however, the radium were produced from the uranium in a direct line without branching, its α-ray activity, calculated from the law that the ionisation is proportional to the two-thirds power of the range of the α-particles, should be 0·57. The value found, 0·488, can only be accounted for if the actinium branch claims either 26 per cent. of the atoms disintegrating if it starts from uranium-*I*, or 14 per cent. if it starts from uranium-*II*. From the proportion of the total activity contributed by the actinium

[67] E. Gleditsch, *Archiv for Mathematik og Naturvidenskab, Christiania,* 1919, **36**, Nr. 1 ; compare A. Fleck, *T.,* 1913, **103**, 384.

[68] S. C. Lind and L. D. Roberts, *J. Amer. Chem. Soc.,* 1920, **42**, 1170 ; *A.,* ii, 463 ; compare Becker and Jannasch, *Jahrb. Radioaktiv.. Elektronik,* 1915, **12**, 1 ; F. Soddy and (Miss) A. F. R. Hitchens, *Phil. Mag.,* 1915, [vi], **30**, 218 ; *A.,* 1915, ii, 726 ; E. Gleditsch, *loc. cit.*

series, estimated from both the new and the old measurements as 0·26 to 0·28 in terms of that of the uraniums as unity, a branching factor of 8 per cent. for the actinium series has hitherto been accepted, but work about to be considered has reduced this to 3 per cent. or less, so that a real inconsistency between the experimental data and our theoretical interpretation exists, the clearing up of which might throw much light on the branching of the series.[69]

The Uranium–Actinium Ratio.—In a study of the pitchblendes of Morogoro and St. Joachimsthal, broeggerite from Norway, and two thorianites from Ceylon, representing extremes of Th/U ratio, the constancy of proportionality between radium, and therefore uranium, and actinium has been confirmed. Since the thorium–uranium ratio varied between the limits of 6×10^{-5} and 6, the independence of actinium and thorium, and the genetic connexion between actinium and uranium, follow.[70]

The Uranium-X–Uranium-Y Ratio.—For uranium derived from the same materials, the constancy of proportionality in the rates of production of uranium-X and -Y was established, and the genetic connexion extended to the supposed first member of the actinium branch series, uranium-Y. In this work, periods of average life for uranium-X_1 of 34·37 days, and for uranium-Y of 35·53 hours, were found. The former is slightly, and the latter considerably, less than the previously accepted values, namely, 35·5 days and 52·8 hours.

The method adopted for separating from uranium the uranium-X_1 and -Y, both being isotopes of thorium, consisted in neutralising the strong uranium solution with sodium hydroxide (not potassium hydroxide or ammonia) and adding a small quantity of a solution of a cerous salt and hydrofluoric acid. The cerous fluoride carries down with it the thorium isotopes, and is redissolved in hydrochloric acid. A milligram of dissolved zirconium is added, and the solution is precipitated with a solution of sodium hydrogen hypophosphate, $NaHPO_3,3H_2O$, according to the method of Koss. This precipitates the thorium isotopes with the zirconium and leaves the cerous salt dissolved. The relative activity of uranium-X_1 and -Y proved to be independent of the source of the uranium, and from it a branching factor for the actinium series of at most 4·2 per cent. was deduced.[71]

[69] *Ann. Reports*, 1909, **6**, 259 ; J. H. L. Johnstone and B. B. Boltwood, *Phil. Mag.*, 1920, [vi], **40**, 50 ; *A.*, ii, 523.

[70] S. Meyer and V. F. Hess, *Sitzungsber. Akad. Wiss. Wien*, 1919, **128**, 2a, 909 ; *A.*, ii, 658.

[71] G. Kirsch, *ibid.*, 1920, **129**, 2a, 309 ; compare M. Koss, *Chem. Zeit.*, 1912, **36**, 686 ; *A.*, 1912, ii, 809.

Parent of Actinium.—Details have been published of the separation of the direct parent of actinium, proto-actinium or ekatantalum, from pitchblende residues.[72] By prolonged and repeated treatment with nitric acid, the other radioactive constituents, including radium, may be almost completely removed. A little tantalum oxide is then added, and the material extracted with hydrofluoric and sulphuric acids. The addition of a few milligrams of thorium and lead nitrates at this stage serves to keep traces of ionium, uranium-X, and radio-lead in the insoluble form. The filtrate is evaporated to dryness, which leaves the tantalum and proto-actinium in an insoluble form, from which impurities, such as iron, zirconia, and the like, may be removed by boiling with aqua regia. So far, all attempts to separate proto-actinium from tantalum have failed.

By various elaborations of this method, the whole of the proto-actinium from pitchblende containing a known amount of uranium was carefully separated, and its α-activity measured. If the branching factor of the actinium series were 8 per cent., the preparation should have an α-activity equal to 4 per cent. of that of the uranium in the mineral. As a mean of six determinations, it was found that the branching factor was only 3 per cent. The completeness of the separation and the avoidance of loss during the chemical treatment were proved by carefully chosen tests with a previously prepared and measured preparation.

Period of Actinium.—From these proto-actinium preparations, a new and independent determination of the life of actinium was arrived at in the following manner. From the known ranges of the six α-rays of the actinium series, including that of proto-actinium, it follows that the initial α-activity of proto-actinium must be in the ratio $1:5\cdot74$ to the α-activity of the substance after equilibrium with the five α-ray-giving members of the actinium series has been attained. The proportionate increase of the α-activity over periods from 400 to 600 days corresponds with a half-period for actinium of 20 years, or to a period of average life of $28\cdot8$ years. This is in good agreement with the further results obtained by observations on the decay of activity of actinium itself, so that the period of actinium may now be regarded as known with reasonable certainty.[73]

[72] *Ann. Reports*, 1918, **15**, 195.
[73] O. Hahn and L. Meitner, *Ber.*, 1919, [B], **52**, 1812; *A.*, ii, 147, 148; *Physikal. Zeitsch.*, 1919, **20**, 529; *A.*, 1919, ii, 209.

Various.

Radioactivity of Rubidium.—An examination of the very feebly penetrating β-activity of rubidium compounds has confirmed the view that it is an atomic property of rubidium, and is unaffected by chemical purification or treatment. The rays are somewhat more penetrating than those of uranium-X_1,

$$[\mu_{A1} = 347 - 308(\text{cm.})^{-1},$$

as compared with 463 for the β-rays of uranium-X_1 and 312 for those of radium]. Their velocity is estimated as 0·6 that of light. The activity is feeble. A surface covered with 0·025 gram of rubidium sulphate per sq. cm. possesses the same activity as one covered with 0·00033 gram of uranium oxide per sq. cm. (total β-rays). Eliminating the penetrating β-rays of uranium-X_2, and extrapolating to a film of zero thickness, so correcting for absorption, it is estimated that the specific activity of the element rubidium is one-fifteenth of that of uranium, due to the change of uranium-X_1. The product of the change, if the normal law is followed, should be an isotope of strontium. It is suggested that the search for calcium, strontium, and cæsium, respectively, in minerals containing potassium, rubidium, and cæsium, and the determination of their atomic weight, if found, might throw further light on the radioactivity of the alkali metals.[74]

Changes in the Radioactivity of the Oxides of Uranium.—Some results in this field incompatible with the present theory of radioactivity have been recorded. The a-activity of various preparations of oxide of uranium showed a diminution over a term of years from 1 to 31 per cent. The greater decreases occurred with the green oxide, prepared by the gentle ignition of ammonium uranate, and the smaller with the black oxide, obtained by strong ignition of the nitrate, preparations of intermediate colour showing intermediate behaviour. In a preparation the a-activity of which had fallen from an initial value 5·95 to 4·64, the initial activity was restored by solution in nitric acid and ignition. It is unfortunate, perhaps, that no changes of weight of the preparations were looked for, for such results might be due to the possible, although hitherto unobserved, gain of oxygen or moisture by the feebly ignited green oxides from the atmosphere. On the other hand, from the impurities separated from the uranium, increases in a-activity from 7 to 93 per cent. were observed, the rate of increase in one case corresponding with a period of 1·1 months.[75]

[74] O. Hahn and M. Rothenbach, *Physikal. Zeitsch.*, 1919, **20**, 194 ; *A.*, 1919, ii, 312. [75] C. Staehling, *Compt. rend.*, 1919, **169**, 1036 ; *A.*, ii, 5.

Period of Ionium.—The minute growth of radium from large amounts of carefully purified uranium, already recorded, has since proceeded regularly according to the square of the time, and a definite estimate of the period of ionium can now be deduced from the measurements. This is the same as that already provisionally calculated. Actually, the product of the periods of average life of ionium and radium alone is involved, and this, to an uncertainty of at most 5 per cent., is 237,500,000 years. The period of ionium is thus 100,000 years if that of radium is 2375 years. The actual growth of radium from 3 kilograms of uranium (element) in 10 years has been 2×10^{-10} gram.[76]

Fractional Crystallisation of Radium and Mesothorium from Barium.—The theory and practice of the enrichment of radium and mesothorium from barium in the fractional crystallisation of the chloride and bromide has been the subject of two communications. The enrichment factor, K, is defined as the ratio of the active material in the crystals to that in the original material in the solution. As regards the chloride, K varies from 1·65 for an acidity 0·25N, with 44 per cent. of the salt crystallising, to 1·49 for an acidity 2N, with 58·3 per cent. crystallising. The condition chosen for study was 0·5N-acidity, with 50 per .cent. crystallising, for which K is 1·62. For the bromide, the value of K fell from 2·60 for 0·25N-acidity and 30 per cent. crystallising, to 2·45 for 1·0N and 38·2 per cent. crystallising. The condition chosen for further study was 0·33N-acidity and 33·3 per cent. crystallising, for which K is 2·5. The enrichment factor is independent of the relative concentration of radium or radium and mesothorium in the solution. From the second communication it appears that, so long as the same fraction of crystals separate, it is independent of acidity. As already known, the bromide offers advantages over the chloride in speed of separation, especially in the earlier stages of the separation. Some evidence was obtained of the formation of a compound, $RaBr_2,2BaBr_2,6H_2O$, as the final product of the fractionation in a weakly acid solution, corresponding with 39 per cent. of anhydrous radium bromide, which would explain the advantage of the chloride over the bromide in the later stages of the purification. On the other hand, in very strongly acid solutions, above 2N, and very small concentration of the radium, below 10^{-7}, the process is actually reversed, and more of the radium remains in the mother liquor than separates out with the crystals.

The most favourable method of carrying on the fractionation

[76] *Ann. Reports,* 1916, **13,** 249 ; F. Soddy, *Phil. Mag.,* 1919, [vi], **38, 483 ;** *A.,* 1919, ii, 443.

in practice is by a system in which the crystals and mother liquors move one step in opposite directions in the series at each crystallisation, except for the fractions enriched above the initial concentration, the mother liquors from which move two steps. In such a system carried out continuously, representing the initial concentration as unity, the series runs as shown, the figures representing the concentrations in each unit of the system: [77]

Mother liquor ⟵ ⟵ ⟵ ⟵ ⟵———— ⟵————

⟵ 0·0016 0·008 0·04 0·20 1·0 2·3 5·0 12·3 27 ⟶

Crystals ⟶ ⟶ ⟶ ⟶ ⟶ ⟶ ⟶ ⟶

In another study of mesothorium–radium–barium bromides, the activities were determined by γ-ray methods. The value of K was found to vary from 2·57 with 24·3 per cent. crystallising to 1·44 with 69 per cent. crystallising.[78]

Solubility of Radium Emanation.—Two series of determinations of the solubility of radium emanation in organic solvents, for the most part, have appeared. The solubility in these is much greater in general than in aqueous liquids, and increases as the hydrocarbon character of the solvent predominates over the aqueous, rising steadily, for example, in a series of aliphatic alcohols or acids.[79] A new determination of the coefficient of diffusion of the radium emanation in water at 14° gave the value 0·82 cm. per day, which corresponds with a molecular diameter of 1·85 Å.[80] The value deduced from the space-lattice of crystals was about two-thirds of this.

γ-Activity of Thorium-D.—The conclusion that in a thorium mineral 36·3 per cent. of the γ-radiation is due to mesothorium-2 and 62·7 per cent. to thorium-D [81] has been confirmed by a comparison of the γ-activities of quantities of the two products in equilibrium with the same quantity of thorium. The γ-activity due to thorium-D was found to be 1·81 times as great as that due to mesothorium-2. Since only 35 per cent. of the thorium atoms disintegrating produce thorium-D, it follows that, atom for atom, thorium-D gives 5·17 times as much γ-radiation as mesothorium-2. From these data, a table of the changes of the γ-activity of a pure mesothorium preparation with time has been constructed. If the

[77] C. E. Scholl, *J. Amer. Chem. Soc.*, 1920, **42**, 889 ; *A.*, ii, 408.

[78] J. L. Nierman, *J. Physical Chem.*, 1920, **24**, 192 ; *A.*, ii, 408.

[79] Alfred Schultze, *Physikal. Zeitsch.*, 1920, **95**, 257 ; *A.*, ii, 577 ; G. Hofbauer, *Sitzungsber. Akad. Wiss. Wien*, 1914, **123**, 2a, 2001.

[80] E. Ramstedt, *Medd. K. Vetenskapsakad. Nobel Inst.*, 1919, **5**, No. 5 ; *A.*, ii, 72.   [81] *Ann. Reports*, 1918, **15**, 220.

initial activity is unity, in three years it is 1·62, and in ten years unity again.[82]

Natural Radioactivity.

Brass.—The improvements in the methods of recording the passage of individual α-particles have been applied to the excessively feeble natural radioactivity of common materials, and have thrown light on the important question whether this is wholly due to known radioactive impurities or is in any part a specific activity. A statistical examination of the α-particles emitted from a hollow brass sphere showed that a large number of the α-particles possessed a very short range, shorter than that of any of the known radio-elements. The rate of emission was one α-particle per sq. cm. of surface in 9·25 hours. The range of this new type was estimated at 1·8 cm. of air. By the Geiger-Nuttall relation, this corresponds with a period of life $1·5 \times 10^6$ times that of uranium. Hence the inference is formed that the α-particles are derived from an actual disintegration of the metal, either copper or zinc, with this excessively long period of 10^{16} years. From copper an isotope of cobalt, and from zinc an isotope of nickel, would result in an α-ray change. It is sad, however, that such elaborate and important physical experiments should be conducted on such a material as—brass!

Rocks.—A survey of the radioactivity of the rocks encountered in the piercing of the Loetschberg Tunnel, which runs from Kandersteg to Goppenstein, in the Bernese Oberland, showed unusual similarity of composition along the length of the tunnel. This agrees with the fact that no abnormal temperature gradient, such as was encountered in the St. Gothard Tunnel, was experienced. The average of all the rocks (eighty-two specimens) was $2·2(\times 10^{-12}$ grams of radium per gram). The rocks at the Kandersteg end are Jurassic limestones, in the centre Gastern granite, and, at the southern end, crystalline schists of all classes. The granites were somewhat lower in radium content, and the calcareous and schistose rocks somewhat higher, than the average for these classes.[83]

The rocks of the Kolar gold field, on the Mysore plateau, southern India, consist of schists of very uniform character, which contain as little radium as, and are probably older than, any rocks known. The temperature gradient in the mines is abnormally

[82] H. N. McCoy and G. H. Cartledge, *J. Amer. Chem. Soc.*, 1919, **41**, 42 *A.*, 1919, ii, 89.
[83] J. H. J. Poole, *Phil. Mag.*, 1920, [vi], **40**, 466 ; *A.*, ii, 657.

low. The average radium content was 0.19×10^{-12} gram per gram.[84]

Spring Waters.—A survey of sixty Canadian mineral springs, and, later, of six hot springs at Banff, Alberta, disclosed only moderate activities. The latter are the most active in Canada, and possess an emanation content of from 2 to $6(\times 10^{-10}$ curie per litre). For the escaping gases, higher values, up to 24, were obtained.[85] The springs of Colorado are exceptionally active, the emanation content for ninety-five exceeding 10, and for five 100. The most active, 305, is surpassed by few European springs.[86]

The sulphur–soda springs of Bagnères-de-Luchon have been found to be the most radioactive in France, and, apart from such waters as actually originate in uranium mines, to be exceeded in activity by less than a dozen in the whole world. The group of some twenty-four springs possessed an emanation content between 4 and 415, five being above 240, and higher than any other French springs.[87]

The principal spring at Bagnoles de l'Orne showed, over a month of observations, variations in emanation content from 2 to 15. Previous observations had given much higher values, 24 in 1907 and 113 in 1904. These variations have been traced to the rainfall. After rain, at an interval varying from six to thirteen days, the springs in this neighbourhood were found to reach a maximum emanation content, the greater the heavier the rainfall. This shows that the activity of the spring is derived from surface waters percolating through radioactive strata and mixing with the deep spring water.[88] Two papers dealing with the practical technique of such measurements have appeared.[89]

The Ocean.—The rate at which radium is supplied to the ocean by rivers and the denudation of the land cannot maintain the quantity present. It follows that there must be in sea-water uranium and ionium in equilibrium proportion to the radium. Taking the mean radium content of sea-water as 1.2×10^{-15} gram per c.c., the uranium must be 4×10^{-6} gram per litre of sea-water, or 0.1 milligram per kilogram of sea-salt. This is about one-tenth of the estimated content of gold in sea-water. On this view, no

[84] H. E. Watson and G. Pal, *J. Ind. Inst. Sci.*, 1914, **1**, 39 ; *A.*, ii, 278.

[85] J. Satterly and R. T. Elworthy, *Trans. Roy. Soc. Canada*, 1917-1918, [iii], **11**, 17, 27 ; **12**, 153 ; *A.*, 1919, ii, 41, 72, 312.

[86] O. C. Lester, *Amer. J. Sci.*, 1918, [iv], **46**, 621 ; *A.*, 1919, ii, 6.

[87] A. Lepape, *Compt. rend.*, 1920, **171**, 731 ; *A.*, ii, 727.

[88] P. Loisel, *ibid.*, 1919, **169**, 791 ; 1920, **171**, 858 ; *A.*, 1919, ii, 489 ; 1920, ii, 727.

[89] O. Nürnberger, *Physikal. Zeitsch.*, 1920, **21**, 198 ; *A.*, ii, 345 ; H Greinacher, *ibid.*, 270 ; *A.*, ii, 463

great variation of radium content with depth is to be anticipated in the ocean. It is calculated that the ocean and the land must be approximately equal factors in maintaining the amount of emanation in the atmosphere, the smaller contribution of the ocean per unit of surface being counterbalanced by its greater area.[90]

The Atmosphere.—At Innsbruck, as the result of forty-nine observations of the emanation content of the atmosphere by the charcoal method, values were obtained between 1110 and 43, with a mean of $433(\times 10^{-15}$ curie per litre), which are considerably above those found in other localities.[91]

It will be recalled that in 1912, during balloon ascents, an increase in the penetrating radiation of the atmosphere was recorded, which became considerable at the height of 3000 metres.[92] Now kite experiments, carried out at the aeronautical observatory of Lindenberg, Prussia, have shown that the active deposit on a wire under the influence of the earth's field is much greater at heights between 1000 and 2500 metres than at the surface. A study of the variations of this from July 29th to December 2nd, 1913 (ninety-eight observations), showed that strong increases occurred with the fall of the barometer. Since, at this height, the supposed explanation of the influence of the fall of the barometric pressure in facilitating the escape of emanation from the surface soil fails, the changes of activity and pressure are regarded as originating in a common cause. A clear parallelism was found to exist between the changes of the activity and what is termed the " potential temperature " of the layer of the atmosphere between 1000 and 2500 metres. By this term is meant the temperature which the air would assume if adiabatically brought to normal pressure. Presumably the changes of this function are independent of internal meteorological influences, and are a measure of the external solar influences. However that may be, temperature changes are supposed to be the cause of the pressure changes, and themselves to originate from a mass radiation from certain limited zones of the solar surface of emanation particles into the upper atmosphere, which owes to this its chief source of heat. Whatever the explanation may prove to be, the study of the radioactivity of the upper atmosphere is clearly likely to lead to important advances.[93]   FREDERICK SODDY.

[90] V. F. Hess, *Sitzungsber. Akad. Wiss. Wien.* 1918, **127**, 2a, 1297.

[91] R. Zlatorovic, *Wien. Anz.*, 1920, 75 ; *A.*, ii, 657.

[92] *Ann. Reports*, 1912, **9**, 327 ; 1913, **10**, 288.

[93] H. Bongards, *Physikal. Zeitsch.*, 1920. **21**, 141 ; *A.*, ii, 277.

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ERRATA.

(ANNUAL REPORTS, 1919.)

Page	Line		
110	10	$\Big\}$ *for* "coumarin" *read* "coumaran."	
111	16		
120	11	" COEt ⟨ ⟩NH " *read* " CH$_2$⟨CH$_2 \cdot$CH$_2$ / CH$_2$–NH⟩CH·CO·CH$_2$·CH$_3$."	

ANNUAL REPORTS

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CONTENTS.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Journal.
A.	Abstracts in Journal of the Chemical Society.*
Acta Med. Scandinav.	Acta Medica Scandinavica.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Ann. Sci. Agron.	Annales de la science agronomique française et étrangère.
Ann. sci. Univ. Jassy.	Annales scientifiques de l'Université de Jassy.
Apoth. Ztg.	Apotheker-Zeitung.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim. Sci.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Pharm.	Archiv der Pharmazie.
Arch.Schiffs u. Tropenhygiene	Archiv Schiffs-und Tropen-Hygiene.
Arkiv. Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei.	Atti della Reale Accademia dei Lincei.
Beibl. Ann. Phys.	Beiblätter zu den Annalen der Physik.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Berl. Klin. Wochenschr.	Berliner Klinische Wochenschrift.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Brennstoff-Chem.	Brennstoff Chemie.
Brit. Med. J.	British Medical Journal.
Brit. Pat.	British Patent.
Bul. Soc. Chim. România	Buletinul Societătei de Chimie din România.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Jard. bot. Buitenzorg.	Bulletin du Jardin botanique de Buitenzorg.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.

* The year is not inserted in references to 1921.

ABBREVIATED TITLE.	JOURNAL.
Bull. Soc. chim. Biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Canadian Chem. J.	Canadian Chemical Journal.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Chem. Listy	Chemické Listy pro vědu a průmysl.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Ztg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
D.R.-P.	Deutsches Reichs-Patent.
Deutsch. Gart. Ztg.	Deutsche Garten-Zeitung.
Eng. and Min. J.	Engineering and Mining Journal.
Fermentforsch.	Fermentforschung.
Gazzetta	Gazzetta chimica italiana
Ges. Abhandl. Kennt. Kohle	Gesammelte Abhandlungen zur Kenntnis der Kohle.
Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Helv. Chim. Acta	Helvetica Chimica Acta.
Int. Z. Metal.	Internationale Zeitschrift für Metallographie.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jap. Pat.	Japanese Patent.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem	Journal of Biological Chemistry.
J. Chem. Ind. Japan (or Tokyo)	Journal of Chemical Industry, Japan.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng Chem.	Journal of Industrial and Engineering Chemistry.
J. Landw.	Journal für Landwirtschaft.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan.	Journal of the Pharmaceutical Society of Japan.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. S. African Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Kolloid Z.	Kolloid Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die Landwirtschaftlichen Versuchs-Stationen.

ABBREVIATED TITLE.	JOURNAL.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Mem. Coll. Sci. Kyōtō	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metall u. Erz	Metall und Erz.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Perf. and Essent. Oil. Rec.	Perfumery and Essential Oil Record.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phillipine J. Sci.	Phillipine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Physiol. Abstr.	Physiological Abstracts.
Proc. Cam. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Gén. Mat. Col.	Revus Générale des Matières Colorantes.
Schweiz. Apoth. Ztg.	Schweizerische Apotheker Zeitung.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Soil Sci.	Soil Science.
Stahl u. Eisen	Stahl und Eisen.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Svensk. Kem. Tidskr.	Svensk Kemist Tidskrift.
T.	Transactions of the Chemical Society.
Texas Agric. Expt. Station Bull.	Bulletins of the Texas Agricultural Experiment Station.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Ver. Deut. Physikal. Ges.	Verhandlungen der deutschen physikalischen Gesellschaft.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. Deut. Öl Fett Ind.	Zeitschrift der deutschen Öl-und Fett-Industrie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. ges. Schiess-u. Sprengstoffw.	Zeitschrift für das gesammte Schiess-und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.

ABBREVIATED TITLE.	JOURNAL.
Z. Kryst. Min. . . .	Zeitschrift für Krystallographie und Mineralogie.
Z. Metallkunde . . .	Zeitschrift für Metallkunde.
Z. Nahr.-Genussm. . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. öffentl. Chem. . .	Zeitschrift für öffentliche Chemie.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem. . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Z. physiol. Chem. . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

ANNUAL REPORTS

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

Specific Heats.

The molecular heat of hydrogen from 0—2600° abs. has been calculated [1] on the basis of Bohr's model of the hydrogen molecule and the assumption that the rotational energy corresponds with *three* degrees of freedom. The molecular energy of gases has been discussed [2] from the point of view of dynamical theory. The increase of specific heat on rise of temperature is assumed to be due to vibrations between the atoms, to which the principle of equipartition does not apply. Equipartition of energy is assumed between each degree of freedom of translation and each effective degree of freedom of rotation. The abnormal behaviour of hydrogen at low temperatures [3] is supposed to be due to a change of molecular structure which deprives the molecule of its two degrees of freedom of rotation. In tri- and poly-atomic gases there is generally a considerable amount of energy of vibration. The conclusion is drawn that the quantum theory is unnecessary, but that the observed facts are not in conflict with it.

The specific heat of nitrogen at 92° abs., corrected for deviations from the gas laws, is almost exactly the equipartition value.[4] The value of dC_p/dp is 0·300 cal./atm.

The velocity of sound in a dissociating gas, such as $N_2O_4 \rightleftharpoons 2NO_2$, has been calculated.[5] It depends on the reaction velocity coefficients, and the latter may be determined in this way.

The internal energy of solids from the point of view of atomic

[1] F. H. MacDougall, *J. Amer. Chem. Soc.*, 1921, **43**, 23; *A.*, ii, 238.

[2] (Sir) J. A. Ewing, *Proc. Roy. Soc. Edin.*, 1920, **40**, 102; *A.*, ii, 299.

[3] Eucken, *A.*, 1912, ii, 232.

[4] R. Bartels and A. Eucken, *Z. physikal. Chem.*, 1921, **98**, 70.

[5] A. Einstein, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 380; compare F. Keutel, *Diss.*, Berlin, 1911.

structure has been considered.[6] Further measurements of specific heats at low temperatures have been determined with a modified form of Nernst and Schwers's apparatus.[7] The results are in most cases in good agreement with Debye's formula.[8] The velocity of sound in air, nitrogen, carbon dioxide, methane, and ethane, at temperatures up to 1000° has been determined by a direct method.[9] The true molecular heats at constant volume are calculated : air $4\cdot8 + 0\cdot0004T$; nitrogen $4\cdot775 + 0\cdot00042T$; carbon dioxide $6\cdot30 + 0\cdot00205T + 0\cdot0000007T^2$; methane $6\cdot66 + 0\cdot019t$; ethane $9\cdot04 + 0\cdot0183t$.

The difference of the molecular heats of a gas has been calculated by three new equations : [10] $C_p - C_v = 0\cdot000087/d_cv_c = 0\cdot0935L/T'$ $= 0\cdot0935p_c/T_cd_c$. The symbols denote : critical density d_c, critical volume v_c, critical temperature T_c, boiling point T', latent heat L, and the third equation is derived from the relation $L = p_cT'/T_cd_c$.[11] The equation of state of D. Berthelot seems, however, to be particularly adapted to such calculations,[12] except at very low temperatures.[13]

An apparatus for the measurement of the velocity of sound in small quantities of gas at different temperatures is described.[14]

Molecular Structure.

Several calculations of molecular diameters from the viscosities of gases have been made.[15] In size and shape the atoms of monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table, the dimensions of which have been deduced indirectly from X-ray crystal measurements. A chlorine molecule may be regarded as having the size and shape of two argon atoms in contact, that is, with their external electron shells touching each other. Gaseous bromine is similarly related to double krypton atoms, and iodine to xenon. An oxygen molecule has the same size and shape as two neon atoms in contact. The shape of a molecule composed of

[6] F. Skaupy, *Z. Physik*, 1921, **4**, 100; *A.*, ii, 300.

[7] Paul Günther, *Ann. Physik*, 1920, [iv], **63**, 476; *A.*, ii, 16.

[8] *A.*, 1912, ii, 1134.

[9] H. B. Dixon, C. Campbell, and A. Parker, *Proc. Roy. Soc.*, 1921, [*A*], **103**, 1; *A.*, ii, 621.

[10] W. Herz, *Z. Elektrochem.*, 1921, **27**, 125; *A.*, ii, 299.

[11] *A.*, 1919, ii, 494.

[12] Compare W. Rücker, *Ann. Physik*, 1921, **65**, 393.

[13] Schimank, *Physik. Z.*, 1916, **17**, 393.

[14] F. Himstedt and R. Widder, *Z. Physik*, 1921, **4**, 355.

[15] A. O. Rankine, *Proc. Roy. Soc.*, 1921, [*A*], **98**, 360, 369, 331; *A.*, ii, 192, 192, 489; compare *Phil. Mag.*, 1921, [vi], **42**, 615.

two equal atoms is assumed to be a spheroid, the volume of which is equal to the sum of the volumes of the hard elastic spheres to which each participating atom is equivalent. The nitrogen molecule is equivalent to a hard, elastic body nearly spherical in shape. The close similarity between the physical properties of nitrous oxide and carbon dioxide again appears from viscosity measurements : their molecules appear to have the same size and shape, and possess an external electron arrangement practically the same as that of three neon atoms in line and contiguous. The diameter of the outer electron shell of cyanogen is nearly equal to that of bromine, as found from crystal measurements. This agrees with the equality of the molecular volumes of potassium bromide and cyanide, and with the assumptions of Lewis [16] and Langmuir [17] with regard to the similarity of the nitrogen and cyanogen molecules. Non-spherical molecules, built up of atoms of unequal sizes, have also been considered.[18] The increases in diameter in passing from neon to ammonia, argon to phosphine, and krypton to arsine are approximately equal, and may represent the effect of the addition of the three nuclei of the hydrogen atoms added to complete the electron configuration of the corresponding inert atom. The calculations are based on Chapman's modification of Sutherland's formula : $4\pi\sigma^2 = 0.491(1 + \epsilon)\rho\bar{V}/\sqrt{2}\nu\eta(1 + C/T)$, where σ = radius of molecule ; ρ = density ; $\bar{V}$ = mean speed ; ν = no. of molecules per c.c., η = viscosity, ϵ is practically = 0, C is a constant, T = abs. temperature.

The symmetrical shapes of polyatomic molecules assumed in such calculations as the above introduce difficulties in other departments of physical measurement, particularly in connexion with the molecular heats. This matter has been discussed [19] and the formulæ of water, hydrogen sulphide, and ammonia deduced from the theory of Lewis [16] assuming distortion of the octets. In water, the linking angle is approximately the same as that between carbon bonds. The distance between the oxygen nucleus and the hydrogen nuclei is the same in both cases, but is different from that between the two hydrogen nuclei. The two hydrogen atoms lie in one half of the resulting tetrahedron and two electron pairs in the other half, expressing the dipolar character of water. An asymmetric structure favours association.

The structure of molecules has also been considered [20] on the

[16] *A.*, 1916, ii, 310.   [17] *Ibid.*, 1919, ii, 328.

[18] A. O. Rankine, *Proc. Physical Soc.*, 1921, **33**, 362; *A.*, ii, 584; *Phil. Mag.*, 1921, [vi], **42**, 601.

[19] E. J. Cuy, *Z. Elektrochem.*, 1921, **27**, 371; *A.*, ii, 584.

[20] G. Kirsch, *Z. physikal. Chem.*, 1920, **96**, 471; *A.*, ii, 193.

basis of Kossel's hypothesis.[21]   The stability of the nitrogen mole-
cule is due to the additional nucleus, and the similarity of the
–CN group to halogens (see above) is due to this cause.   Similar
stabilising nuclei are assumed to be present in the molecules of
carbon monoxide, ozone, oxides of nitrogen, and the –CNO
radicle.

The cubical atom theory has been considered [22] from the point
of view of internal structure, and the radii of atoms have been
calculated.   The electronic affinities and heats of formation can
also be satisfactorily found.[23]

The collision between molecules and free electrons has been
studied.[24]   In the case of slow electrons (1 volt) it was found that
the electron is either absorbed outright, or not in any way influenced
as regards its direction and velocity by the gas molecule.   For
every atom or molecule there seems to be a fixed sphere of action,
outside which a slow electron is not influenced, but inside which
it is strongly influenced.   A law of force of rapidly diminishing
continuous distance action is regarded as improbable.   Argon shows
deviations, and is also peculiar in exhibiting selective absorption.

Molecular volumes have been considered [25] from the point of view
of the Lewis-Langmuir theory, and particularly the theory of
isosteres.   Isosteric molecules and nuclear atoms in hydrogen
compounds are shown to have the same volume.   The latter
depends on the number and arrangement of the electrons sur-
rounding the nucleus rather than on the charge on the latter.
Nitrogen and carbon monoxide molecules probably have a normal
acetylenic structure, three pairs of electrons being shared, rather
than the condensed structure suggested by Langmuir (see above).

An interesting theory of colour in relation to molecular structure
has been put forward.[26]   In some cases, an atom of large atomic
volume is unable to form a stable octet by taking an electron from
an atom of small atomic volume, in which the attraction between
the kernel and electrons is greater.   An unstable orbit, which may
be disturbed by light, then results.   It has been known for some
time that compounds in which an atom is unsaturated, or in which

[21] *A.*, 1916, ii, 243.

[22] A. Landé, *Z. Physik*, 1920, **2**, 87;   *A.*, ii, 189;   *ibid.*, 380;   *A.*, ii, 189;
E. Madelung and A. Landé, *ibid.*, 230;   *A.*, ii, 190;   H. Schwendenwein, *ibid.*,
1921, **4**, 73;   *A.*, ii, 310.

[23] See *Ann. Reports*, 1920.

[24] H. F. Mayer, *Ann. Physik*, 1921, [iv], **64**, 451;   *A.*, ii, 234;   C. Ramsauer,
ibid., 513;   *A.*, ii, 324;   O. Klein and S. Rosseland, *Z. Physik*, 1921, **4**, 46;
A., ii, 291.

[25] R. N. Pease, *J. Amer. Chem. Soc.*, 1921, **43**, 991;   *A.*, ii, 437.

[26] J. Meisenheimer, *Z. physikal. Chem.*, 1921, **98**, 304;   *A.*, ii, 364.

two atoms of the same element exhibit different valencies, are usually coloured.

When the atomic diameter is calculated from b of van der Waals's equation by the formula $\sigma = (3b/2\pi N)^{\frac{1}{3}}$, where $N = 2\cdot75 \times 10^{19}$, the increase in passing from one inert gas to another is constant ($0\cdot28 \times 10^{-8}$ cm.). This relation is not obtained when σ is calculated from the viscosities; it is in agreement with Langmuir's theory.[27] The atomic radii of helium, neon, argon, krypton, and xenon are supposed, on the basis of theoretical considerations,[28] to be in the proportion $3:4:6:7:8$. The true radii of the atoms are multiples of one " elementary length," $0\cdot036$ to $0\cdot039$ Å.

An ingenious calculation of the absorption spectrum of hydrogen chloride from the quantum theory of molecular rotations [29] lends support to the existence of the two isotopes of chlorine.

Surface Tension.

Further investigations of thin films on water have been made.[30] Any further quantity of oleic acid, placed on water already covered with a layer of thickness double that which corresponds with the maximum extension, does not undergo spontaneous extension, but forms globules. The layer is then regarded as " saturated." If the surface occupied by a given quantity of oleic acid is reduced, the tension decreases and then suddenly becomes constant. An improved technique for the investigation of thin films on water has been described.[31] The compressibility curves of the film are accurately straight lines, with a doubtful deviation at very low compressions. An abrupt change in the properties of the film takes place at an acidity of $10^{-5}N$, under compression less than 16 dynes/cm. The area occupied by each molecule becomes about 20 per cent. greater than on neutral solutions. Langmuir's view [32] that the films consist of a single layer of molecules, with the carboxyl groups turned towards the water, is confirmed and extended. Different films, and even different parts of the same

[27] L. St. C. Broughall, *Phil. Mag.*, 1921, [vi], **41**, 872; *A.*, ii, 445.

[28] M. Pierucci, *Nuovo Cim.*, 1921, [vi], **22**, 189; *A.*, ii, 583; compare *A.*, 1920, ii, 538.

[29] A. Kratzer, *Z. Physik*, 1920, **3**, 460; *A.*, ii, 140; *ibid.*, 289; *A.*, ii, 142. Compare W. L. Bragg and H. Bell, *Nature*, March 24, 1921; *A.*, ii, 689; G. Hettner, *Z. Physik*, 1920, **1**, 345; *A.*, ii, 144; E. S. Imes, *Astrophys. J.*, 1919, **50**, 251; *A.*, ii, 4; A. Haas, *Z. Physik*, 1921, **4**, 68; *A.*, ii, 286; F. W. Loomis, *Astrophys. J.*, 1920, **52**, 248; *A.*, ii, 530.

[30] A. Marcelin, *Compt. rend.*, 1921, **173**, 38; *A.*, ii, 488. Compare *Ann. Physique*, 1913.

[31] N. K. Adam, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 336; *A.*, ii, 488.

[32] *A.*, 1917, ii, 525.

film, vary considerably in their resistance to collapse on compression. The latter seems to be aided by nuclei.   A mutual influence between saturated and unsaturated molecules in the same film has been detected.[33]

The adhesional work, W_A, between mercury and organic liquids has been calculated [34] by the formula $W_A = \gamma_1 + \gamma_2 - \gamma_{12}$, where γ_1 and γ_2 are the free surface energies of the two liquids and γ_{12} the free surface energy of the interface.   In some cases the latter is negative,[35] and the surfaces rise in temperature when they are formed.   The liquids which show this abnormal behaviour in contact with water are heptinene, n- and sec.-octyl alcohols, and heptaldehyde.   Addition of oxygen increases the tensile energy feebly, whilst the adhesional energy towards water is largely increased.   Double bonds show the opposite effects.   The facts are explained on the assumption that unsymmetrical molecules are oriented in the surface.   Oxygen atoms turn towards the water. The length of a hydrocarbon chain is of more importance in determining the solubility than the nature of the active group at the end of the molecule.   The triple bond has a greater relative effect on the adhesional energy than on the adhesional work at 20° as compared with a hydroxyl oxygen atom.

The surface tension of mercury in a vacuum at various temperatures has been determined by the drop method [36, 37] and the interfacial tensions between mercury and a number of organic liquids have been found by the same method.   The adhesional work between mercury and an organic liquid is always greater than between water and the liquid, or between the liquid and itself.   It decreases rapidly with increase of temperature, whilst the total energy increases.

The statical measurement of interfacial tension, and the relation between interfacial tension and surface tension in organic solvents in contact with aqueous solutions have been described.[38]

By combining Trouton's rule with the Eötvös expression, the relation $L = 20\gamma/S^{\frac{2}{3}}M^{\frac{2}{3}}$, where L = latent heat, M = molecular weight, γ = surface tension at the boiling point and S = density at the boiling point, has been deduced.[39]   This holds approximately

[33] P. Woog, *Compt. rend.*, 1921, **173**, 387; *A.*, ii, 575.

[34] W. D. Harkins and E. H. Grafton, *J. Amer. Chem. Soc.*, 1920, **42**, 2534; *A.*, ii, 87.

[35] W. D. Harkins and Y. C. Cheng, *ibid.*, 1921, **43**, 35; *A.*, ii, 242; compare *A.*, 1920, ii, 357.

[36] W. D. Harkins and W. W. Ewing, *ibid.*, 1920, **42**, 2539; *A.*, ii, 87.

[37] J. Palacios, *Anal. Fís. Quím.*, 1920, **18**, 294; *A.*, ii, 304.

[38] W. C. Reynolds, *T.*, 1921, **119**, 460, 466.

[39] W. Herz, *Z. Elektrochem.*, 1921, **27**, 25; *A.*, ii, 300.

for normal, but not for associated, liquids. From this the molecular diameter d may be calculated by the formula $d = 1/10(M/S)^{\frac{1}{3}} \cdot 0 \cdot 00102/42700$. The internal pressure is calculated by the formula $B = L/2v = 10\gamma/(Mv)^{\frac{1}{3}} \times 42700/1033$, where Mv is the molecular volume. The following values were found : benzene 1830 atm., ethyl acetate 1425 atm., aniline 2120 atm.

The latent heat may also be calculated from the critical data by the equation $L = 0 \cdot 00093 T_s/d_c v_c$, where T_s is the absolute boiling point, and d_c and v_c are the critical density and volume, respectively.[40] From the Trouton rule it follows that $M \times 0 \cdot 00093/d_c v_c$ must be constant. This is approximately the case with normal liquids.

It has been shown [41] that if the glass is properly cleaned, and evaporation of liquid prevented, the supposed finite contact angle in the measurement of the surface tensions of some organic liquids does not exist. The correction for the capillary rise in wide tubes calculated by Laplace and Rayleigh was also verified.[42]

The effect of adsorbed gases on the surface tension of water has been found; the surface tension is diminished by an amount which is greater the higher the density of the gas, except for carbon dioxide.[43]

The relation $1/\beta J = -2\lambda_1 s$, in which λ_1 is the internal latent heat, β the compressibility, and s the specific gravity, of a liquid, has been deduced [44] from van der Waals's equation on the assumption that a is independent of volume. If a depends on volume, $1/\beta J = \epsilon\lambda_1 s$, where $\epsilon = \rho/\alpha$ and $\rho = 1/\sigma \cdot \partial\sigma/\partial T$, the coefficient of variation of surface energy σ with temperature; $\alpha = 1/v \cdot \partial v/\partial T$. The first equation is approached at higher temperatures, the second at lower temperatures. J is the mechanical equivalent of heat.

The equation $MLJ = \pi\gamma d^2 N + RT$, where d is the molecular diameter, γ the surface tension, and N Avogadro's number, has been deduced [45] for the latent heat of evaporation. The values of d calculated agree with those found by Bragg, or from kinetic theory. Vaporisation is considered as a discontinuous change, the elementary quantity of energy concerned being $10 \times 10^{-16}T$ ergs. The value of K in $\pi\gamma d^2 N = K(T_c - T)$ agrees with that from Eötvös's law. The connexion between Trouton's rule and Wien's

[40] W. Herz, Z. Elektrochem., 1921, 27, 26; A., ii, 300; compare A., 1919, ii, 494.

[41] T. W. Richards and E. C. Carver, J. Amer. Chem. Soc., 1921, 43, 827; A., ii, 384; compare A., 1915, ii, 522.

[42] Compare also S. Sugden, T., 1921, 119, 1483.

[43] S. S. Bhatnagar, J. Physical Chem., 1920, 24, 716; A., ii, 169; compare also reference [41].

[44] D. L. Hammick, Phil. Mag., 1921, [vi], 41, 21; A., ii, 84; compare Lewis, Z. physikal. Chem., 1911, 78, 24.

[45] R. Audubert, Compt. rend., 1921, 172, 375; A., ii, 240.

displacement law, $\lambda_m T =$ const., has also been pointed out.[46]   The latent heat of evaporation is given by $L = Nh\nu$, where h is Planck's constant, and ν a frequency, but the critical energy increment is an average value.   The formula is obtained as follows : $\lambda_m T_c = 0\cdot28986$; $\nu = c/\lambda_m$ ($c =$ velocity of light); hence $L = Nh\nu = Nhc T_c/0\cdot28986 = 9\cdot866 T_c$.

The latent heats of fusion per gram-atom of the inactive gases have been calculated.[47]   The value of Eucken's measurement [48] of the latent heat of fusion of argon, $0\cdot268$ kg.cal., is used.   The following values were found : helium $< 0\cdot004$; neon, $0\cdot08$; krypton, $0\cdot33$; xenon, $0\cdot43$; niton, $0\cdot65$.

Properties of Liquids ; Association.

The constants a and b of van der Waals's equation may be calculated, in the case of normal liquids, from the number of atoms in the molecule, n; the number of valencies in the molecule, z; the critical data, and other constants.[49]   The following equations were deduced for the constant b : $b = 412n10^{-6} = 201z10^{-6} = 795\cdot16 \times M^2 10^{-4}/T_s^2 d_s = 12354 d_s 10^{-3}/p_c^2$.   The constant a is calculated from the equations : $a = 5\cdot094n T_c 10^{-6} = 2\cdot49z T_c 10^{-6} = 4\cdot5846n^2 p_c 10^{-6} = 1474\cdot713 M^2 10^{-6}/T_s d_s = 23992 d_s T_s 10^{-6}/p_c^2$.   The coefficient of expansion of normal liquids may be calculated from a and b.

The " constant " a in Thorpe and Rücker's formula for the dependence of specific volume on temperature : [50] $V_0/V_t = (a T_c - T)/(a T_c - 273)$ is shown to decrease with increasing temperature.[51] In most series of analogous substances, a increases with the molecular weight; with the exception of the value for water it lies between $1\cdot5$ and $2\cdot1$.

In the case of organic liquids containing carbon, hydrogen, and oxygen, the relation $n = 193 M^2/T_s^2 d_s$ has been deduced by Groshans. If this is combined with the relation $n = 1\cdot1 T_c/p_c$ and with Trouton's rule, it follows [52] that $M/T_s^2 = 0\cdot00077$.   This holds with approximate accuracy for compounds ranging from ethane ($T_s = 187\cdot6$) to anthraquinone ($T_s = 653$).   By combining Groshans's equation with the relation $v_c = 0\cdot0009n$, it is shown that $v_c = 0\cdot1737 M^2/T_s^2 d_s$, or from the above equation, $v_c = 1\cdot34 \times 10^{-4} M/d_s$.   The values of

[46] E. K. Rideal, *Phil. Mag.*, 1921, [vi], **42**, 156; *A.*, ii, 489.

[47] J. Narbutt, *Physikal. Z.*, 1921, **22**, 52; *A.*, ii, 163.

[48] Eucken, *Beibl. Ann. Phys.*, 1916, **40**, 322.

[49] W. Herz, *Z. Elektrochem.*, 1921, **27**, 373; *A.*, ii, 573.

[50] *T.*, 1884, **45**, 135.

[51] W. Herz, *Z. physikal. Chem.*, 1921, **97**, 376; *A.*, ii, 374.

[52] W. Herz, *Z. anorg. Chem.*, 1921, **116**, 250; *A.*, ii, 484; compare Jorissen, *A.*, 1920, ii, 90; *A.*, ii, 484; compare also *A.*, 1920, ii, 285.

v_c calculated for a number of esters of fatty acids agree well with those observed. The relation between specific heat s and critical data for the higher paraffins can be expressed by $sM = 2 \cdot 44 T_c/p_c$.

The ratio of molecular volume to density is not constant at corresponding temperatures for normal and associated liquids.[53] The ratio d_s/d_c, where d_s and d_c are the densities at the boiling point and at the critical temperature, is $2 \cdot 69$ for monohalogenated benzenes. The assumption of constancy of the ratio of molecular volume to density would give $M_c/M_s = 2 \cdot 69 d_c/d_s$, where M_c and M_s are the molecular weights at the critical temperature and the boiling point. For a number of known associated liquids the ratio was found to be nearly unity. It is concluded that the theory of corresponding states cannot be applied where changes of molecular state occur.

The ratio of the densities of liquid and vapour has been shown to be a function of the reduced temperature T/T_c, and as a first approximation does not depend on the individual properties of the liquid.[54] The value of B in the equation $B = d_l^2/T \log K$, where d_l = density of liquid and $K = d_l/d_v$ is the ratio just referred to, is found to be practically constant for normal liquids. It shows a slight maximum at the point $T/T_c = 0 \cdot 60$ to $0 \cdot 65$ and a slight minimum at the point $T/T_c = 0 \cdot 85$ to $0 \cdot 90$. In the case of associated liquids, the value of B increases with temperature and exhibits no maximum or minimum.

The equation of Mendeléev : $D_t = D_0(1 - Kt)$, where D_0 and D_t are the densities of a liquid at $0°$ and $t°$, and K is a constant, has been tested with benzene, its halogen substitution products, and mixtures of these.[55] It represents the facts equally for normal and for associated liquids, within the limits of experimental error, and cannot be used to differentiate between the two groups. The constant K for mixtures can probably be calculated by the mixture rule.

Hydrogen has been found to obey the law of rectilinear diameter.[56] The critical density is calculated as $0 \cdot 03$ at $-239 \cdot 91°$.

A relation between the critical data and the chemical constant has been deduced.[57] The chemical constant is calculated by the equation $C = \lambda_0/4 \cdot 571 T$, where $\lambda = (\lambda_0 + AT - BT^2 - \ldots)$

[53] W. Herz, Z. anorg. Chem., 1921, **115**, 237; A., ii, 436.

[54] W. Swientoslawski, Bull. Soc. chim., 1921; [iv], **29**, 499; A., ii, 535; ibid., 507; A., ii, 536.

[55] W. Herz and J. Meyer, Z. physikal. Chem., 1921, **97**, 381; A., ii, 381.

[56] E. Mathias, C. A. Crommelin, and H. K. Onnes, Compt. rend., 1921, **172**, 261; A., ii, 256.

[57] Fr. A. Henglein, Z. anorg. Chem., 1920, **114**, 234; A., ii, 163; Z. physikal. Chem., 1921, **98**, 1.

$(1 - p/p_k)$ is the latent heat and p_k, T_k are the critical constants. Nernst's equation, $C = 0.14\lambda/T_B$, where T_B is the absolute boiling point, follows from van der Waals's equation, $\log p/p_k = a(1 - T_k/T)$. Cederberg's equation, $C = k \log p_k$ (where k is 1·6 in many cases), also follows from this equation, since it is a special case of the more general equation, $C = 1.1 \log p_k/(T_k/T_B - 1)$.

The critical temperature of mercury has been calculated,[58] from the change of surface tension with temperature, as 1474°. Another calculation [59] from theoretical considerations gave 1700°, the critical pressure being estimated at 1100 atm.

If in van der Waals's vapour pressure equation the critical temperature is replaced by the expression $\frac{1}{2}(1/K_{20} + 293)$, where K_{20} is the coefficient of expansion at 20°, the value of the constant a is close to, generally greater than, 3 for a number of esters. The critical pressure p_c in the same equation can be replaced by $1/K_{20} + 293/0.88n$, where n is the sum of the valencies of the constituent atoms. The constant in Cederberg's formula (see above) has an abnormally high value for organic compounds, increasing with the molecular weight.[60]

The equation $p = RT(d_1 + d_2)(d_2/d_1)^{(d_1 + d_2)/(d_1 - d_2)}$, where p is the vapour pressure, and d_1 and d_2 are the densities of liquid and vapour, has been deduced.[61] The quantity $d_1 + d_2$ may be regarded as a density factor which is a measure of the cohesive forces per unit mass.

Radiation and the Quantum Theory.

The interpretation of the chemical constant, as given by Nernst and by Sackur, has been criticised.[62] The chemical constants of zinc (1·62) and cadmium (1·56) have been calculated [63] by Nernst's formula. These differ somewhat from the values obtained by Egerton,[64] from whose results they are deduced, but agree with the value 1·59 given by the Sackur-Stern-Tetrode formula. The theory of the chemical constant, from the point of view of statistical mechanics, has been considered,[65] and the quantum theory has been applied to the theory of corresponding states.[66] An expression is

[58] G. Meyer, *Physikal. Z.*, 1921, **33**, 76; *A.*, ii, 238.

[59] J. J. van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 267, 282; *J. Chim. Phys.*, 1920, **18**, 273; *A.*, ii, 83.

[60] W. Herz, *Z. Elektrochem.*, 1921, **27**, 125; *A.*, ii, 302.

[61] J. H. Shaxby, *Phil. Mag.*, 1921, [vi], **41**, 441; *A.*, ii, 239.

[62] E. Yamazaki, *J. Tokyo Chem. Soc.*, 1920, **41**, 19; *A.*, ii, 574.

[63] G. Heidhausen, *Z. Elektrochem.*, 1921, **27**, 69; *A.*, ii, 240.

[64] *A.*, 1920, ii, 84.

[65] W. Schottky, *Physikal. Z.*, 1921, **22**, 1; *A.*, ii, 179.

[66] A. Byk, *ibid.*, 15; *A.*, ii, 163.

obtained which represents the physical properties of the liquid state, and covers the abnormalities observed with substances of small molecular weight.

In the application of the quantum theory to evaporation,[67] two formulæ may be used : (1) $L = Nh(v_2 - v_1)$, where v_1 and v_2 are the frequencies of the solid or liquid and of the vapour, respectively; (2) $L = \frac{1}{2}Nh\{v_5 - (v_3 + v_4)\}$ where v_3, v_4, and v_5 are the frequencies of activation cf the positive nucleus, of the electron, and the radiation frequency, respectively.

On the basis of the similarity between evaporation and solution, it has been suggested [68] that Trouton's rule should have an analogue in solution, $\lambda/T = const.$, where λ is the molecular heat of solution and T the temperature which corresponds, for a state of saturation, with an osmotic pressure of 1 atm. By extrapolation from the results with a number of salts, the value was found to be 30—32. From this the elementary quantity of energy involved when a molecule passes into solution was calculated as $18 \times 10^{-16} . T$ ergs, which is the same as that found for the energy of dissociation of solids and of sublimation.

The applications of statistical methods to chemical equilibria have been reported.[69] The theory of the velocity of unimolecular reactions from the point of view of the radiation hypothesis has been critically discussed.[70] It is concluded that the similarity in form between the Arrhenius formula, giving the dependence of reaction velocity on temperature, and Wien's law, for the intensity of radiation as a function of temperature, is purely accidental. The absence of absorption bands where they would be indicated by the hypothesis of activating frequencies, and the fact that the energy available, in the form of radiation, is very much less than required, are urged against the hypothesis. A modification of the radiation hypothesis has been proposed [71] which meets some of the objections. The dependence of the unimolecular reaction constant on temperature can be fairly satisfactorily represented by the expression $k = se^{- Q/RT}$, but the significance of s and Q have been differently interpreted.[72] It is suggested that Q represents the difference between the energy of the reacting molecules and the *average* energy of all the molecules of that kind. The

[67] E. K. Rideal, *Proc. Camb. Phil. Soc.*, 1921, **20**, 291; *A.*, ii, 431.

[68] R. Audubert, *Compt. rend.*, 1921, **172**, 676; *A.*, ii, 303.

[69] K. F. Herzfeld, *Physikal. Z.*, 1921, **22**, 186; *A.*, ii, 313.

[70] I. Langmuir, *J. Amer. Chem. Soc.*, 1920, **42**, 2190; *A.*, ii, 31; compare also M. Polányi, *Z. Physik*, 1920, **3**, 31; *A.*, ii, 179.

[71] R. C. Tolman, *J. Amer. Chem. Soc.*, 1921, **43**, 269; *A.*, ii, 248.

[72] Compare W. C. McC. Lewis, *T.*, 1918, **113**, 471; Lewis and A. McKeown, *J. Amer. Chem. Soc.*, 1921, **43**, 1288; *A.*, ii, 623.

theoretical conclusions are confirmed by an investigation [73] of the photochemical decomposition of nitrogen pentoxide. The frequency corresponding with the critical increment may be calculated from the effect of temperature on the reaction velocity according to the equations : $d \log_e K/dT = E/RT^2$ and $E = Nh\nu$,[74] but light of this frequency is found not to decompose nitrogen pentoxide. In presence of nitrogen dioxide, however, light of 400—460 $\mu\mu$ accelerates the decomposition of the pentoxide, but this does not take place without the dioxide, or in the dark in presence of dioxide. It is suggested that the nitrogen dioxide acts as a photo-catalyst by absorbing radiation, transforming it through fluorescence and giving it out at a particular frequency which is effective in bringing about the decomposition of the pentoxide. The experimental verification of this hypothesis would certainly lend valuable support to the radiation theory of catalysis.

The quantum theory of chemical reaction leads to the equation $k_1 = \nu e^{-Q/RT}$ for the velocity constant of a unimolecular reaction,[75] where ν is a frequency and Q the heat of activation. It is assumed that $Q = Nh\nu$, which agrees with the experimental results on the decomposition of phosphine. For bimolecular reactions the equation :

$$k_2 = N\sigma^2\sqrt{8\pi RT(1/M_A + 1/M_B)}e^{-\frac{Q_A + Q_B}{RT}}$$

is deduced, where σ is the mean molecular diameter, M_A and M_B the molecular weights, of A and B, and $Q_A + Q_B$ the total heat of activation. This agrees with experiment. Investigation of the influence of the solvent on the temperature coefficient of reaction velocity has been found,[76] in the case of similar solvents, in some sense to support the deduction from the radiation hypothesis that there is an inverse proportionality between velocity and temperature coefficient. This does not hold for dissimilar solvents. These are not regarded as simple catalysts, and " the radiation theory does not apply to such cases." Tolman's criticisms of Marcelin's deduction of the equation for reaction velocity (see above) has been examined [77] and its validity questioned.

Einstein's photochemical equivalence law, $n = Q/h\nu$, where n = no. of molecules decomposed, Q = energy absorbed, ν = fre-

[73] F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53, 72; *A.*, ii, 249. Compare E. C. C. Baly and W. F. Barker, *T.*, 1921, **119**, 662.

[74] J. Perrin, *A.*, 1919, ii, 177; W. C. McC. Lewis, *T.*, 1918, **113**, 471.

[75] S. Dushman, *J. Amer. Chem. Soc.*, 1921, **43**, 397; *A.*, ii, 315.

[76] H. E. Cox, *T.*, 1921, **119**, 142.

[77] E. P. Adams, *J. Amer. Chem. Soc.*, 1921, **43**, 1251; *A.*, ii, 628.

quency, has been confirmed [78] for the reactions between bromine and *cyclo*hexane (gaseous) and chlorine and trichlorobromomethane (liquid). The latter was found to be a good " acceptor " for activated chlorine molecules. A solution of chlorine in the liquid on exposure to light probably undergoes the following reactions :

$$Cl_2 + CBrCl_3 + h\nu = CCl_4 + Cl + Br;$$
$$Cl + CBrCl_3 + Br = CCl_4 + Br_2.$$
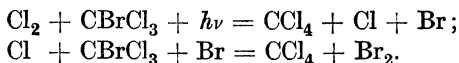
The bromine could be determined spectrophotometrically; the radiation absorbed was determined by a thermopile as usual. The phenomena are explained on Bohr's theory as follows : a quantum $h\nu$ is absorbed by the chlorine molecule, the valency-electron springs to a larger ring, and the molecule is activated. This active state has a given " life " (calculated as 10^{-10} secs.), during which it may react with àn acceptor. If no acceptor is present, the activated molecule gives up energy in the form of other quanta (luminescence, or heat), or transfers it to indifferent molecules, causing a general rise of temperature.

Physical Properties and Chemical Composition.

Some empirical relations between the absolute critical temperature, boiling point, and. melting point [79] have been shown [80] to be purely arithmetical and to have no physical meaning. New relations are deduced from van der Waals's formula $\log p/p_c = f(T_c/T - 1)$, where f may depend slightly on the temperature. If T_1 = boiling point, $p = 1$ atm., then $\phi_1 = T_c/T = \log p_c/f + 1$. ϕ_1 will therefore be approximately constant unless p_c is abnormal (helium). In the case of fusion, $(v_2 - b_2)/v_2 = 1/14$, where $v_2 - b_2$ is the effective volume for molecular motion. Thence $\phi_2 = T_c/T_2 = 2a_c/\gamma a_2$, where T_2 = m. p., a = attraction constant, γ is usually 0·9 but for ideal substances (a and b constant) is 0·5. For ordinary substances, $a_2 = 1·4a_c$; $\phi_2 = 2$. For limiting substances (with T_c from 400° to 500°), $\phi_2 = 1·83$, which agrees with the rule of Timmermans [81] that the melting points of different families of substances tend to an upper limit of 117°.

The cause of the alternate higher and lower melting points of successive members of the fatty acid series has been explained [82]

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[78] W. Noddack, *Z. Elektrochem.*, 1921, **27**, 359; *A.*, ii, 568; see also E. C. C. Baly and W. F. Barker, *T.*, 1921, **119**, 653, for a study of the reaction $H_2 + Cl_2 = 2HCl$. •

[79] M. Prud'homme, *J. Chim. phys.*, 1920, **18**, 270, 307, 359; *A.*, ii, 83, 84, 376.

[80] J. J. van Laar, *J. Chim. phys.*, 1921, **19**, 4; *A.*, ii, 622.

[81] *A.*, ii, 430.

[82] G. Tammann, *Z. anorg. Chem.*, 1919, **109**, 221; *A.*, 1920, ii, 285.

on the hypothesis that acids with an even number of carbon atoms exist in two stable crystalline forms. In support of this, it was shown that acetic acid exists in two forms with a triple point at $57\cdot5°$ at 2330 kilos. per sq. cm. No isomerism was found with formic acid. Attention is now [83] directed to the obvious insecurity in basing such a general theory on two observations. It is shown that many other physical properties show the same kind of alternation in homologous series. When the numerical value of the property (solubility, molecular rotation, boiling point) is plotted against the number of carbon atoms, the points corresponding with an even number of carbon atoms lie on one smooth curve, and those corresponding with an odd number on another. These regularities may be explained on the hypothesis [84] of the alternate positive and negative character of carbon atoms in a chain. The theory of isomerism, however, is obviously· still open to experimental confirmation.[85]

The relation between heats of combustion and constitution has been discussed.[86] Symmetrical nitro-compounds appear to be most stable.

Guldberg's rule, that the (absolute) boiling point at 1 atm. is equal to two-thirds of the critical temperature, is approximately correct. Atmospheric pressure, however, is not a constant fraction of the critical pressure, and an attempt has been made [87] to test the relationship at fractions $\frac{1}{33}$ and $\frac{1}{50}$ of the critical pressure. With organic liquids $\frac{1}{50}$ gave better results, but with inorganic liquids (water, nitrogen, hydrogen sulphide) the constant was lower than with organic liquids.

A linear relation $y = \alpha x + a$ has been found [88] to hold between the molecular volume y of one haloid salt and the corresponding volume x of another haloid, the two salts containing a common kation or anion. The question is raised whether the crystalline structure of cæsium haloids is the same as that of the other alkali haloids. The distance between oppositely charged ions in haloid salts is calculated as $r = 0\cdot938 \times 10^{-8} \sqrt[3]{V}$ cm., where V is the molecular volume of the salt.

[83] E. J. Cuy, *Z. anorg. Chem.*, 1921, **115**, 273; *A.*, ii, 429.

[84] *Idem*, *J. Amer. Chem. Soc.*, 1920, **42**, 503; *A.*, 1920, i, 361. Compare A. Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, (iii), 1; *A.*, ii, 543; M. T. Hanke and K. K. Koessler, *J. Amer. Chem. Soc.*, 1918, **40**, 1726; *A.*, 1919, i, 4.

[85] Compare Tammann, *Z. anorg. Chem.*, 1921, **115**, 288; "*A.*, ii, 430.

[86] O. H. Binder, *Chem. Zeit.*, 1921, **45**, 477; *A.*, ii, 435; W. E. Garner and C. L. Abernethy, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 213; *A.*, ii, 435; compare *T.*, 1921, **119**, 6.

[87] R. Lorenz and W. Herz, *Z. anorg. Chem.*, 1921, **115**, 100; *A.*, ii, 433.

[88] K. Fajans and H. Grimm, *Z. Physik*, 1920, **2**, 299; *A.*, ii, 168.

Theory of Mixtures.

The vapour pressures of liquid mixtures have been considered [89] from the thermodynamic point of view, and it is shown that the assumption of chemical combination is unnecessary in many cases to explain the results. Evidence of chemical combination was found with sulphuric acid and ethyl ether.

The thermodynamic theory of mixtures,[90] and the theory of Dolezalek [91] have also been further discussed. An attempt has been made [92] to apply the latter theory to the electromotive behaviour of alloys.

Electrolytic Conductivity ; Ionisation.

The abnormality of strong electrolytes has been further considered. On the assumption that interionic forces in solution are inverse square functions of the distances apart of dissimilar ions, and that the forces causing dissociation are inverse higher power functions of the distances between molecules, an interpretation of some types of dilution law is obtained.[93] Complete ionisation is not assumed, and the law of mass action holds good if active mass is represented by a momentum term. The assumption that the abnormality is due to the abnormal osmotic behaviour of the ions is in entire agreement with the fundamental assumptions made.

The theory of Ghosh [94] has been further criticised. It is shown [95] that in his calculation of the number of ions having kinetic energies in excess of a given value (" free ions "), Ghosh has used an incorrect formula. When the correct expression is used, the results are no longer in good agreement with experiment.

The dielectric constants of some electrolytic solutions have been determined.[96] The electrolytes lowered the dielectric constant of water in a way similar to that of the majority of non-electrolytes.

The limiting value of the molecular conductivity, λ_{∞}, in non-

[89] A. W. Porter, *Trans. Faraday Soc.*, 1921, **16**, 336; *A.*, ii, 377.

[90] M. B. Wagner, *Z. physikal. Chem.*, 1920, **96**, 287; 1921, **97**, 229, 330, 337, 343; *A.*, ii, 162, 300, 375; compare *A.*, 1920, ii, 596, 597.

[91] *A.*, 1909, ii, 22; 1913, ii, 482; H. Cassel, *Z. Physik*, 1920, **2**, 146; *A.*, ii, 166; A. Schulze, *Z. physikal. Chem.*, 1921, **97**, 388, 417; *A.*, ii, 388, 390.

[92] F. Clotofski, *Z. anorg. Chem.*, 1920, **114**, 1; *A.*, ii, 203.

[93] W. Hughes, *Phil. Mag.*, 1921, [vi], **42**, 134, 428; *A.*, ii, 481, 573.

[94] *T.*, 1918, **113**, 449, 627, 707, 790; compare *Ann. Reports* for 1918 and 1919.

[95] D. L. Chapman and H. J. George, *Phil. Mag.*, 1921, [vi], **41**, 799; *A.*, ii, 371; compare H. Kallmann, *Z. physikal. Chem.*, 1921, **98**, 433.

[96] R. T. Lattey, *Phil. Mag.*, 1921, [vi], **41**, 829; *A.*, ii, 426.

aqueous and aqueous solutions has been discussed.[97] According to the Ostwald-Bredig rule, the value of λ_∞ is related to λ_v, at the dilution v, by the formula $\lambda_\infty = \lambda_v + d_v$, where d_v is a constant depending only on the dilution. If the value of λ_∞ is calculated by the formula $\lambda_\infty = \lambda_v + b'/v^{0.45}$,[98] the values of d_v can be calculated for each solvent for different dilutions. It was found that the Ostwald-Bredig rule can be applied to water and fifteen organic solvents through the range of dilutions $v = 256$ to $50,000$. From general considerations, it was deduced that the product $d_v \cdot \epsilon \cdot \eta_\infty$ should be constant at a particular dilution for all solvents, ϵ being the dielectric constant and η_∞ the viscosity. This was confirmed, and it was further found that by introducing the dilution factor $v^{0.45}$ an expression is obtained which is general for all solvents (including water) and solutes at all dilutions : $d_v \cdot \epsilon \cdot \eta_\infty \cdot v^{0.45} =$ const. $= 51.4$. Thus, if ϵ and η_∞ are known for the solvent, d_v can be calculated for any dilution. Thence, from a single observation of λ_v, the value of λ_∞, and from it $\alpha = \lambda_v/\lambda_\infty$, can be found. It is shown [99] that the product $\lambda_\infty \eta_\infty$ is constant for all ionising solvents; it is independent of the temperature between $0°$ and $25°$, but depends, within limits, on the nature of the solute. The above general expression may be written $(1 - \alpha)\epsilon \cdot v^{0.45} = 51.4/\lambda_\infty \eta_\infty =$ const., which shows that, if $\lambda_\infty \eta_\infty$ is known for a salt in any one solvent, its degree of ionisation in any other solvent at any dilution may be calculated. The diameters of ions in aqueous solutions have been calculated [1] from Einstein's diffusion formula : $U = K/N \cdot 6\pi\eta\rho$, where $U =$ velocity, $\rho =$ radius, of particle, $K =$ force acting on particle, $N =$ Avogadro's number, $\eta =$ viscosity. For most ions, ρ lies between 2.0×10^{-8} cm. and 3.9×10^{-8} cm., but is abnormal for hydrogen (1.1×10^{-8}) and lithium (4.7×10^{-8}). The ionic radii in non-aqueous follow the same order as in aqueous solutions : $H^· < K^· < Ag^· < Na^· < Li^·$; $Br' < I' < Cl' < NO_3'$, but in the former the values are about twice as great (mean values 2.67 and 5.33×10^{-8} cm.). Organic anions and kations have the same radius in both solutions (4.4×10^{-8}). Much greater solvation in non-aqueous solutions is assumed.

The sizes of the ions in crystal lattices, calculated by a modification of Born's theory, were found to be,[2] in 10^{-8} cm. :—Na 0.517; K 0.794; Rb 0.914; F 0.75; Cl 0.953; Br 1.021; I 1.122. The energies of the alkali haloid lattices, in kg. cal., were calculated :

[97] P. Walden, *Z. anorg. Chem.*, 1920, **113**, 113; *A.*, ii, 170; *ibid.*, 1921, **115**, 49; *A.*, ii, 423.

[98] R. Lorenz, *A.*, 1920, ii, 6.

[99] P. Walden, *Z. anorg. Chem.*, 1920, **113**, 85; *A.*, ii, 160.

[1] P. Walden, *ibid.*, 125; *A.*, ii, 171.

[2] K. Fajans and K. F. Herzfeld, *Z. Physik*, 1920, **2**, 309; *A.*, ii, 174.

NaF 210·4; NaCl 170·0; NaBr 159·7; NaI 146·7; RbBr 146·5; RbI 135·8.

The theory of Hertz has been further developed.[3] The value of Hertz's " constant," A, is not 18·9, but is different for each ion. The radii of a number of ions are calculated.

The electrolytic conductivities of a number of molten salts, at temperatures to 1600° have been determined.[4]

The radius of an ion may be calculated [5] from the formula $W = \frac{1}{2}(1 - 1/\epsilon)N \cdot 2388 \times 10^{-11}e^2z^2/r_i$ Cal., where W = heat of hydration,[6] N = Avogadro's constant, z = valency, e = charge on electron, r_i = radius of ion, ϵ = dielectric constant of solvent. The values of r_i and of r_a (the atomic radius) are calculated, and it is shown that (except in the case of thallium) for positive ions $r_i < r_a$, whilst for negative ions $r_i > r_a$. This is explained by the increase in volume in the formation of negative ions by the absorption of an electron into the atomic structure, and the decrease in volume when a positive ion is formed by removal of an electron from the atom.

The dissociation of ternary electrolytes has been investigated [7] in the cases of sulphuric, oxalic, and tartaric acids, and the normal and hydrogen salts of these acids with thallium and potassium. Solutions of concentrations below $0·04N$ follow the law of mass action, and in certain cases this holds at even higher concentrations.

The ionisation of tetramethylammonium thiocyanate (a strong electrolyte) is practically the same ($\alpha = 0·38$) in saturated solutions in nine non-aqueous solvents.[8] The solubility of the same salt in different non-aqueous solvents is, approximately, given by $\epsilon/\mu^{\frac{1}{3}} = 34$, where ϵ = dielectric constant, μ = molecular solubility.

The " objection " to the electrolytic dissociation theory due to Kahlenberg, and quoted in most text-books, is shown [9] to rest on inaccurate experiments. Benzene solutions of salts of organic acids (copper oleate, barium erucate, copper stearate, and silver melissate),

[3] R. Lorenz, *Z. anorg. Chem.*, 1920, **113**, 131; *A.*, ii, 158; *ibid.*, 135; *A.*, ii, 158; R. Lorenz and P. Osswald, *ibid.*, 114, 209; *A.*, ii, 158; R. Lorenz and W. Neu, *ibid.*, 1921, **116**, 45; *A.*, ii, 481; R. Lorenz and W. Michael, *ibid.*, 161; *A.*, ii, 482; R. Lorenz and A. Scheuermann, *ibid.*, 121, 140; *A.*, ii, 482, 483; compare *Ann. Reports*, 1920.

[4] F. M. Jaeger and B. Kapma, *ibid.*, 1920, **113**, 27; *A.*, ii, 160.

[5] M. Born, *Z. Physik*, 1920, **1**, 45; *A.*, ii, 166.

[6] See *Ann. Reports*, 1920; A. von Weinberg, *Z. Physik*, 1920, **3**, 337; *A.*, ii, 165; A. Reis, *ibid.*, 1920, **1**, 294; *A.*, ii, 166.

[7] C. Drucker, *Z. physikal. Chem.*, 1920, **96**, 381; *A.*, ii, 161.

[8] P. Walden, *Z. Elektrochem.*, 1921, **27**, 34; *A.*, ii, 309.

[9] H. P. Cady and E. J. Baldwin, *J. Amer. Chem. Soc.*, 1921, **43**, 646; *A.*, ii, 309.

which give precipitates with dry hydrogen chloride, showed a conductivity before and during reaction.

Evidence of the ionisation of gases during chemical change has been obtained,[10] in the cases : $Cl_2 + 2NO = 2NOCl$; $2O_3 = 3O_2$; and the reaction between ozone and nitric oxide or nitrogen dioxide.

Electromotive Forces

The use of a saturated KCl-calomel electrode has been proposed [11] for use in $E.M.F.$ measurements in place of $0.1N$- and N-calomel electrodes. On the assumption that the absolute potential of the N-calomel electrode at 25° is 0.5648 volt, that of the saturated potassium chloride electrode is 0.5266 volt, with a temperature coefficient of $+ 0.00020$ volt/degree from 5° to 60°. A saturated salt bridge is used.

The hydrion concentration in pure water has been found [12] to be 1.23×10^{-8} by a method depending on charging a condenser first with the cell $Hg|HgCl,KCl|KCl|H_2O|H_2$, and then with a standard cell, and in each case discharging through a galvanometer.

Further measurements of the heat of formation of silver iodide by $E.M.F.$ methods have been made.[13] The discrepancy between the results of Fischer [14] and of Jones and Hartmann [15] has been shown to depend on the uncertainty in the correction for I_3' ions in the potassium iodide solution, this being now determined experimentally, and on the use of electrochemically purer silver electrodes by Fischer. The value 15,158 cal. is obtained, which, compared with Fischer's value of 15,169 cal. and that of Jones and Hartmann (14,570), points to the greater accuracy of the former value.

The effect of fluorescent dyes on the $E.M.F.$ of illuminated cells has been studied,[16] both alone and in presence of oxidising and reducing substances. The Becquerel effect was observed, and the behaviour of the cells can be explained on the hypothesis of a concealed oxygen–hydrogen photolysis. This has been confirmed [17] by using a fluorescent substance in an electrolytic cell, when a depolarising action was clearly noticed.

The thermodynamic treatment of concentrated solutions, with

[10] A. Pinkus and M. de Schulthess, *J. Chim. phys.*, 1920, **18**, 366; *Helv. Chim. Acta*, 1921, **4**, 288; *A.*, ii, 368; compare O. W. Richardson, *Phil. Trans.*, 1921, [*A*], **222**, 1; *A.*, ii, 422.

[11] H. A. Fales and W. A. Mudge, *J. Amer. Chem. Soc.*, 1920, **42**, 2434; *A.*, ii, 79.

[12] H. T. Beans and E. T. Oakes, *ibid.*, 2116; *A.*, ii, 12.

[13] O. Gerth, *Z. Elektrochem.*, 1921, **27**, 287; *A.*, ii, 534.

[14] *A.*, 1912, ii, 536, 1054.

[15] *Ibid.*, 1915, ii, 308.

[16] E. Staechelin, *Z. physikal. Chem.*, 1920, **94**, 542; *A.*, 1920, ii, 580.

[17] E. Baur, *Z. Elektrochem.*, 1921, **27**, 72; *A.*, ii, 236.

special reference to the $E.M.F.$'s of amalgams, has been developed.[18] The electromotive properties of a number of binary alloys have been studied.[19] With thallium and thallium–lead alloys, the potentials with 0 to 20 atom. per cent. of lead are practically equal to those of thallium; from 50 to 100 atom. per cent. of lead ,they are equal to the lead potentials; between 20 and 50 atom. per cent. of lead the potentials pass into one another asymptotically.

Experiments on thermo-elements [20] showed that copper–phosphorus alloys did not give a favourable ratio of thermal to electrical conductivity, which is inversely proportional to the efficiency of a thermo-couple. Antimony–cadmium alloys with approximately atomic composition show probably the highest thermoelectric power of all metals and alloys hitherto investigated. The influence of heat treatment is of importance in investigating the effect of temperature on $E.M.F.$ Amalgamation depresses thermoelectric power. The effect of pressure on a solid junction of two materials has been calculated [21] on the assumption of material transport with the current. The measurement of the resulting " bary-electromotive force " would give the transport numbers in solid electrolytes and the ratio of electronic to material conduction in poor conductors.

Chemical Dynamics and Equilibrium.

An investigation [22] of the catalytic decomposition of hydrogen peroxide by sodium iodide in aqueous mixtures of alcohols, glycerol, and pyridine failed to disclose any relation between the velocity of reaction and the dielectric constant, viscosity, or surface tension of the pure solvent; the latter appears to exert a specific influence. The effect of mercuric ions on the velocity of oxidation of arsenious acid by nitric acid is peculiar.[23] At a concentration of 7.7×10^{-6} mol. per litre the reaction was completely inhibited. With diminishing concentration, the inhibiting effect of the mercuric ions became less marked down to a concentration of 7.7×10^{-8},

[18] G. N. Lewis and M. Randall, *J. Amer. Chem. Soc.*, 1921, **43**, 233; *A.*, ii, 241.

[19] R. Kremann, *Z. Metallkunde*, 1920, **12**, 185; *Chem. Zentr.*, 1920, iii, 684; *A.*, ii, 10; R. Kremann and H. Ruderer, *ibid.*, 1920, **12**, 209; *Chem. Zentr.*, 1920, iii, 684; *A.*, ii, 11; R. Kremann and J. Gmachl-Pammer, *Int. Z. Metal.*, 1920, **12**, 241; *Chem. Zentr.*, 1921, i, 123; *A.*, ii, 156.

[20] G. Pfleiderer, *Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 409; *Chem. Zentr.*, 1921, i, 348; *A.*, ii, 296; F. Fischer and G. Pfleiderer, *ibid.*, 440; *Chem. Zentr.*, 1921, i, 349; *A.*, ii, 296.

[21] M. Polányi, *Z. physikal. Chem.*, 1921, **97**, 459; *A.*, ii, 372.

[22] Van L. Bohnson, *J. Physical Chem.*, 1920, **24**, 677; *A.*, ii, 185.

[23] A. Klemenc and F. Pollak, *Z. anorg. Chem.*, 1921, **115**, 131; *A.*, ii, 442.

and at 7.7×10^{-9} there was a positive catalytic effect, which became still more marked at 7.7×10^{-11} mol. per litre. The smallest measured effective concentration of catalyst previously recorded is 7×10^{-6} for colloidal platinum in the decomposition of hydrogen peroxide.

The kinetics of the reduction of azo-compounds by acid stannous chloride has been studied.[24] The reaction is bimolecular, and in cases where the azo-compound is broken up into two amino-derivatives it occurs in two stages. The reduction to hydrazo-compound takes place first with measurable velocity; further reduction then occurs with extreme rapidity.

The kinetics of the formation of acetone from acetoacetic acid in acid and in alkaline solution has been studied.[25] In the second case, practically only the anion $CH_3 \cdot CO \cdot CH_2 \cdot CO_2'$, whilst in strongly acid solution practically only undissociated acetoacetic acid, is present. The undissociated and dissociated acids show very different velocities of decomposition; that of the former is fifty times the greater. In almost neutral solutions, the rate of decomposition depends on the ionisation of the acid.

Many reactions having large temperature coefficients are sensitive to light,[26] hence it is concluded that sensitiveness to temperature and to light influences have a common cause, in agreement with Perrin's radiation hypothesis.[27]

A number of abnormally large and small temperature coefficients have been explained [28] by hydrolysis of some salt present. The reaction between iodic acid and potassium iodide in dilute solutions is very rapid at $0°$. In presence of sodium and magnesium sulphates, slightly less iodine is liberated at higher than at lower temperatures. This apparent negative coefficient is due to hydrolysis of the sulphate at higher temperatures, with formation of OH' ions. The abnormally large temperature coefficient of the reaction $3I_2 + 6OH' = 5I' + IO_3' + 3H_2O$ in presence of sodium carbonate and sodium hydrogen carbonate is due to hydrolysis of these salts.

A study [29] of induced reactions led to the hypothesis that the substance in which oxidation is induced (sodium arsenite) acts as a negative catalyst towards the substance which induces the

[24] H. Goldschmidt and A. Braanaas, *Z. physikal. Chem.*, 1920, **96**, 180; *A.*, ii, 184.

[25] E. M. P. Widmark, *Acta Med. Scandinav.*, 1920, **53**, 393; *Chem. Zentr.*, 1921, i, 9; *A.*, ii, 183.

[26] N. R. Dhar, *Proc. K. Akad. Wetensch. Amsterdam,* 1920, **23**, 308; *A.*, ii, 37.

[27] *A.*, 1919, ii, 177.

[28] N. R. Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 313; *A.*, ii, 37.

[29] *Idem, ibid.*, 1921, **23**, 1074; *A.*, ii, 391.

oxidation (sodium sulphite). The formation of a complex of the two oxidisable substances, the less oxidisable constituent of which is more easily oxidised, is assumed.

In a study of the keto-enolic tautomerism of benzoylcamphor,[30] it was found that the results obtained by K. H. Meyer's method [31] of titration with bromine do not agree with the equation $c_A/c_B = Kl_A/l_B$, where c_A, c_B are the equilibrium concentrations, l_A, l_B the solubilities, and K is a constant independent of the nature of the solvent.[32] When the method of optical activity [33] was used, a satisfactory agreement was found, and the ratios of the enol/ketone forms in equilibrium in different solvents were found to be : in toluene, 82/18; in alcohol, 61/39; in acetone, 52/48. At − 83°, both forms should co-exist in the crystalline state.

A new method for the determination of the vapour pressure of salt hydrates is described.[34] It consists in the establishment of equilibrium between the hydrates and a solution of water in iso-amyl alcohol, followed by an estimation of the water content of the resulting liquid. · (With salts of small vapour pressure, a simple method would appear to be a determination of the freezing point of benzene in equilibrium with the salt.)

Variations with time in the activity of colloidal platinum have been studied.[35] The catalytic power is attributed to a metal–oxygen complex, and the initial rise of activity to increase of oxygen concentration. The oxide theory is also supported by other workers.[36]

The conditions which control the accuracy of titration of mixtures of acids and bases, from the point of view of suitable choice of indicator, have been described.[37]

The increase in size of particles of a precipitate in contact with a liquid is usually ascribed to the (experimentally verified) difference in solubility of large and small crystals. It has been suggested [38] that it is due to " irreversible transformation of secondary aggre-

[30] H. Vixeboxse, *Rec. trav. chim.*, 1921, **40**, 1; *A.*, ii, 179.

[31] *A.*, 1911, i, 350, 832.

[32] Van't Hoff, quoted by Dimroth, *A.*, 1911, ii, 31; 1913, ii, 763; compare Smits, *A.*, 1915, ii, 750.

[33] M. O. Forster, *T.*, 1901, **79**, 987.

[34] R. E. Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 704; *A.*, ii, 376; A. A. Noyes and L. R. Westbrook, *ibid.*, 726; *A.*, ii, 377.

[35] A. de G. Rocasolano, *Compt. rend.*, 1921, **173**, 41, 234; *Anal. Fís. Quím.*, 1920, **18**, 308, 361; 1921, **19**, 114; *A.*, 1920, ii, 479, 607; 1921, ii, 251, 321, 390, 498, 542.

[36] R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1921, **54**, [*B*], 113; *A.*, ii, 185.

[37] H. T. Tizard and A. R. Boeree, *T.*, 1921, **119**, 132.

[38] S. Odén, *Svensk. Kem. Tidskr.*, 1920, **32**, 108; *A.*, ii, 25.

gates primarily formed." Reversibility appears to depend on the degree of hydration of the particles which are attached to one another by aqueous envelopes. If these are broken, or if the original hydration is too slight (for example, with metallic particles) the transformation becomes irreversible.

The effect of one solute, A, in lowering the solubility of a second solute, B, in a given solvent has been shown to be represented [39] by the simple equation log $(s_0/s) = kc$, where s_0, s are the solubilities of B in the pure solvent and in a solution of A in B of concentration c, and k is a constant.

Heterogeneous Reactions.

The influence of physical conditions on the velocity of decomposition of some crystalline solids was investigated [40] in the cases of the evolution of gas by heat from silver permanganate, potassium permanganate, ammonium dichromate, and solid solutions of potassium permanganate and potassium chlorate. The conclusion is drawn that the rate of decomposition is largely dependent on the surface of the solid, that the effective surface is considerably greater than the apparent surface, and that solid crystals may be assumed to be aggregates loosely held together. The results with solid solutions support the hypothesis that the process of solid mixture leads to increased chemical stability, from the heat of mixture.

The reduction of cotton-seed oil by hydrogen in presence of metallic nickel at 180° [41] shows that the variations in catalytic power of reduced nickel may be referred to the different surfaces of nickel exposed. In the catalytic reduction of ethylene to ethane in presence of nickel, an induction period was noticed,[42] followed by a sharp maximum velocity. It is supposed that hydrogen is selectively adsorbed, whilst ethylene is adsorbed only after activation (chiefly by "thermal contact" with a molecule undergoing hydrogenation). The nickel at first becomes covered with hydrogen molecules. Reaction of these with ethylene molecules occurs, the heat liberated being communicated to the surrounding molecules. Hydrogen is then volatilised and activated ethylene deposited.

The relation between the occlusive power of palladium for hydrogen and its catalytic activity has been studied,[43] lead being

[39] P. C. L. Thorne, *T.*, 1921, **119**, 262; compare W. Nernst, *Z. physikal. Chem.*, 1890, **6**, 16.

[40] C. N. Hinshelwood and E. J. Bowen, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 203; *A.*, ii, 443; compare *Phil. Mag.*, 1920, [vi], **40**, 569; *A.*, 1920, ii, 743.

[41] E. F. Armstrong and T. P. Hilditch, *ibid.*, 490; *A.*, 1920, ii, 582.

[42] D. M. and W. G. Palmer, *ibid.*, 402; *A.*, ii, 541.

[43] E. B. Maxted, *T.*, 1921, **119**, 1280.

the inhibitant. The relation is linear from the point corresponding with zero concentration of the poison up to a stage where the greater part of the activity has been suppressed. In this region a point of inflexion occurs, beyond which the rate of decrease in catalytic activity due to further addition of lead falls off much less rapidly than on the main part of the curve. The amount of lead required to reduce the catalytic activity to half is very much less than that which reduces the occlusive power to half its original value. This may be explained by the fact that, whilst the occlusion is not confined to the surface, catalysis is mainly a surface phenomenon. Measurements of the adsorption of gases by metallic catalysts [44] show that it is a specific property of the metal, depending on the mode of preparation, being less the higher the temperature to which the metal has been subjected. Destruction of catalytic activity is accompanied by almost complete suppression of adsorptive power. Maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. A strong or irreversible adsorption of any one of the reacting substances tends to render the catalyst inactive. Reaction is the resultant of two factors, adsorption and temperature. The adsorptive capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong, a lower temperature may effect interaction.

Combustion and Explosion Reactions.

The mechanism of reaction in some cases of combustion has been studied [45] and the conclusion is drawn that reaction is preceded by the formation of an unstable additive compound. The minimum amount of moisture necessary to promote explosion of carbon monoxide with oxygen or nitrous oxide corresponds with a partial pressure of 0.5 mm. The reaction is formulated as follows : (1) $CO + H_2O = H \cdot CO_2H$; (2) $H \cdot CO_2H = CO_2 + H_2$; (3) $H_2 + O_2 = H_2O_2$; (4) $H_2O_2 = H_2O + O$. The presence of hydrogen in the carbon monoxide flame was proved by its passage through palladium. Hydrogen peroxide was detected when the gas was passed through a heated quartz tube, cooled in the further part. An indication of a peroxide-like substance was also obtained in the combustion of cyanogen.

The influence of carbon dioxide on the pressure limit of phosphorescence of phosphorus in oxygen and on the inferior limits of explosion of hydrogen and methane is greater than that of

[44] H. S. Taylor and R. M. Burns, *J. Amer. Chem. Soc.*, 1921, **43**, 1273; *A.*, ii, 630.

[45] H. von Wartenberg and B. Sieg, *Ber.*, 1920, **53**, [*B*], 2192; *A.*, ii, 107.

nitrogen.[46] The point of inflammation of various mixtures of hydrogen and oxygen, defined as the temperature at which the reaction velocity exceeds a measurable value, has been measured [47] by bringing both gases to the required temperature and determining by a membrane manometer whether rapid reaction occurs on mixing. The minimum inflammation point, 397·5°, was found with $3H_2 + 2O_2$; for $H_2 + O_2$ it is 407°, and increases after the minimum to 433° for $4H_2 + O_2$ (in all cases for dry gases). With moist gases, the results were rather irregular. The reaction between moist oxygen and hydrogen is bimolecular; with absolutely dry gases, it would seem to be termolecular. The possibility of velocity measurements is discussed.

A detailed study of the propagation of combustion in gaseous mixtures from the point of view of Hugoniot's law has appeared.[48] The phenomenon of successive explosions has also been investigated.[49] Measurements of the heat loss by conduction and radiation during the explosion and subsequent cooling of mixtures of coal gas and air indicate [50] that at the moment of maximum pressure about 10 per cent. of the heat of combustion has not been converted into thermal energy and that after-burning continues for at least 0·25 sec. after the attainment of the maximum pressure.

Reference may be made to the important monograph on the properties of explosives contributed in a special lecture to the Society.[51]

A piezoelectric method of measuring explosion pressures has been described.[52]

The modes of ignition of mixtures of hydrogen and of carbon monoxide with oxygen have been studied [53] by measurements of the rate of rise of pressure. In the second case, there is a slower rise of pressure and evolution of heat for a relatively long time after the attainment of the maximum pressure.

Colloids.

Determinations of the radii of ultramicroscopic gold and silver particles (a) from the colour, (b) from the Brownian movement,

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[46] W. P. Jorissen, *Rec. trav. chim.*, 1920, **39**, 715; *A.*, ii, 99; compare *A.*, 1919, ii, 62.

[47] H. Fiesel, *Z. physikal. Chem.*, 1921, **97**, 158; *A.*, ii, 317.

[48] L. Crussard, *Technique moderne*, 1920, **12**, 243, 295; *A.*, ii, 32.

[49] A. Stavenhagen and F. Schuchard, *Z. angew. Chem.*, 1920, **33**, 286; *A.*, ii, 33.

[50] W. T. David, *Proc. Roy. Soc.*, 1921, **98**, [A], 303; *A.*, ii, 85.

[51] (Sir) R. Robertson, *T.*, 1921, **119**, 1.

[52] D. A. Keys, *Phil. Mag.*, 1921, [vi], **42**, 473; *A.*, ii, 628.

[53] W. A. Bone and W. A. Haward, *Proc. Roy. Soc.*, 1921, [A], **100**, 67; *A.*, ii, 628.

showed no systematic variation between the two series.[54] The degree of dispersity of sols with particles so small as to be invisible in the ultramicroscope may, as is known,[55] be found by allowing the particles to act as nuclei for the deposition of gold. This method of " gilding " hås been [56] applied to determine the radius of amicrons. Smoluchowski's formula [57] for the velocity of flucculation is verified [58] for the rapid, but not for the slow, flocculation of a selenium sol. The limiting size of a particle which exhibits Brownian movement has been found [59] to be $2 \cdot 6\mu$ for a number of metals. In different liquids, the logarithm of the limiting size was found to give a straight line when plotted against the viscosity : $a\eta^{0 \cdot 229} = 3 \cdot 5$ for gold; $a\eta^{0 \cdot 249} = 3 \cdot 4$ for copper.

A series of investigations on soap curds [60] has confirmed and extended the ultramicroscopic investigations of Zsigmondy and Bachmann.[61] It is shown that soap may exist in three distinct hydrated forms : sol and gel (transparent) and curd (opaque).

The physical-chemical analysis of ferric hydroxide sols shows [62] that this substance is a complex salt of the type $x\mathrm{Fe(OH)}_3 y\mathrm{Fe/An}$, where An is the anion in presence of which the sol is formed.

The modulus of rigidity of gelatin gels at different concentrations, under torsion, follows Hooke's law nearly up to the breaking point.[63] The modulus of elasticity, E, and the concentration, c, are related by $E = kc^n$ over a limited range, but the constants k and n differ for different grades of gelatin. The elasticity is not a simple function of the hydrogen-ion concentration. Gelatin gels may represent any transition stage between a two-phase structure and a physically homogeneous system in which mechanical strength must be attributed to solution forces.

Three-phase emulsions may be obtained [64] by shaking pairs of immiscible liquids, such as water and benzene, with alumina, zinc

[51] R. Fürth, *Physikal. Z.*, 1921, **33**, 80; *A.*, ii, 243.

[55] Zsigmondy, *A.*, 1906, ii, 679.

[56] G. Börjeson, *Kolloid Z.*, 1920, **27**, 18; *A.*, ii, 27.

[57] *A.*, 1917, ii, 297.

[58] H. R. Kruyt and A. E. van Arkel, *Rec. trav. chim.*, 1920, **39**, 656; *A.*, ii, 25 (compare *A.*, 1919, ii, 140; 1920, ii, 739); *ibid.*, 169; *A.*, ii, 312.

[59] B. Arakatsu and M. Fukuda, *Mem. Coll. Sci. Kyoto*, 1920, **4**, 179; *A.*, ii, 175.

[60] J. W. McBain, W. F. Darke, and C. S. Salmon, *Proc. Roy. Soc.*, 1921, [*A*], **98**, 395; *A.*, ii, 312; McBain and M. E. Laing, *T.*, 1920, **117**, 1506; McBain and H. E. Martin, *ibid.*, 1921, **117**, 1369; McBain and Salmon, *ibid.*, 1374.

[61] *A.*, 1913, ii, 194.

[62] W. Pauli, *Kolloid Z.*, 1921, **28**, 49; *A.*, ii, 246.

[63] S. E. Sheppard and S. S. Sweet, *J. Amer. Chem. Soc.*, 1921, **43**, 539; *A.*, ii, 311.

[64] H. Bechold, L. Dede, and L. Reiner, *Kolloid Z.*, 1921, **28**, 6; *A.*, ii, 177.

dust, or yeast, and an " emulsion promoter," such as pyridine, acetic acid, ethyl alcohol, or sodium nitrate. The relative surface tensions of the two liquids have no influence on the emulsification.

The influence of the concentration of a sol on the coagulative power of any given ion has been investigated.[65] For univalent ions, the concentration to produce coagulation increases with decreasing concentration of the colloid, very rapidly at low values of the latter. For bivalent ions, the ion concentration is almost constant, and thus independent of the concentration of the colloid. For tervalent ions, the coagulating concentration is almost proportional to the colloid concentration. At least two properties of the system colloid + electrolyte seem to be involved. The influence of dilution and quantity of electrolyte on flocculation has also been considered.[66] The velocity of flocculation, with a constant quantity of electrolyte and colloid, at first diminishes as the dilution of electrolyte increases, but tends to a limit when the dilution reaches a certain value. When the amount of electrolyte is varied but the concentration kept constant, the velocity of flocculation increases with the amount of electrolyte used.

In a study [67] of the swelling of gelatin, it is concluded that the swelling is the result of osmotic pressure within the gel, the latter acting as an imperfectly resisting membrane.

Investigations on proteins [68] show that the Hofmeister series is not the correct expression of the relative effects of ions on the swelling of gelatin. The valency, not the nature, of the ion in combination with gelatin affects the degree of swelling. Results depend on the effect of the salt added on the hydrogen-ion concentration of the protein solution.

The electro-endosmose of a number of solutions with various membranes has been investigated.[69] The charge on which the electro-endosmosis depends can be attributed to ionic adsorption.

The precipitation of colloids by electrolytes has been considered [70] from the point of view of the surface forces exerted by heteropolar crystal lattices on adsorbed ions. The results were confirmed by measurements of the adsorption of thorium-B by silver haloids. Those ions are strongly adsorbed by an ionic space lattice which

[65] E. F. Burton and E. Bishop, *J. Physical Chem.*, 1920, **24**, 701; *A.*, ii, 176.

[66] A. Boutaric and M. Vuillaume, *Compt. rend.*, 1921, **173**, 229; *A.*, ii, 537.

[67] C. R. Smith, *J. Amer. Chem. Soc.*, 1921, **43**, 1350;, *A.*, i, 749.

[68] J. Loeb, *J. Gen. Physiol.*, 1920, **3**, 247; *A.*, i, 136; *ibid.*, 1921, **3**, 391; *A.*, i, 367; compare *A.*, 1920, i, 894.

[69] A. Gyemant, *Kolloid Z.*, 1921, **28**, 103; *A.*, ii, 298.

[70] K. Fajans and K. von Beckerath, *Z. physikal. Chem.*, 1921, **97**, 478; *A.*, ii, 386.

forms sparingly soluble compounds with the oppositely charged constituent of the lattice.

It has been shown that arsenic trisulphide sols are photochemically active.[71] Colloidal sulphur is formed by exposure to light.

The precipitation of arsenious sulphide sols by cobaltammine ions has been applied [72] to determine the valency of the ions. The limiting concentration of the precipitating solution can be expressed by the formula $S_N = S_1/N^4$, where S_N is the equivalent concentration of an N-valent ion and S_1 the limiting concentration for a univalent ion. This is deduced theoretically from the adsorption formula.

A comparison of the protective effect, and the inhibiting influence on catalytic decomposition, of colloids,[73] has shown that the two are parallel. Soaps are regarded as colloidal even at great dilution.

Adsorption.

Freundlich's rule, that the order in which substances are adsorbed is almost independent of the nature of the solid phase, has been confirmed [74] with various kinds of charcoal. Except in the case of iodine, the adsorption isotherm, $x/m = \alpha c^{1/n}$ was found to hold, the constant α being taken as an index of the adsorptive power. The adsorption of iodine by carbon in different forms, in benzene and chloroform, has been studied [75] over periods of time extending to five years. A rapid condensation of iodine takes place in the first few minutes, followed by a much slower " sorption " continuing for months or years. The first condensation is attributed to true adsorption, the second to slow absorption.

The adsorption of salts by silver powder [76] lends support to Polányi's theory [77] that the adsorbed ions form several molecular layers.

The adsorption equilibrium between fatty acids in aqueous solution and charcoal is displaced [78] by neutral salts in the sense that more acid is adsorbed. The amounts of cation and anion adsorbed by carefully purified charcoal from aqueous solutions of

[71] H. Freundlich and A. Nathansohn, *Kolloid Z.*, 1920, **28**, 258; *A.*, ii, 494.

[72] K. Matsuno, *J. Coll. Sci. Tokyo*, 1921, **41**, ii, 1; *A.*, ii, 637.

[73] T. Iredale, *T.*, 1921, **119**, 109, 625.

[74] I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 630; *A.*, ii, 383.

[75] J. B. Firth, *Trans. Faraday Soc.*, 1921, **16**, 434; *A.*, ii, 382.

[76] H. von Euler and A. H. Hedelius, *Arkiv Kem. Min. Geol.*, 1920, **7**, No. 31, 1; *A.*, ii, 490.

[77] M. Polányi, *Ber. Deutsch. Physik. Ges.*, 1916, **18**, 76; *A.*, 1916, ii, 474.

[78] G. Wiegner, J. Magasanik, and A. J. Virtanen, *Kolloid Z.*, 1921, **28**, 51; *A.*, ii, 244.

alkali nitrates are equivalent in all cases.[79]   The adsorption increases with the atomic weight of the kation, and the same holds with nitrates of alkaline earths.   Experiments with potassium and barium salts showed that the adsorption of halogen anions increases with the atomic weight.   The variation with the kation is not considerable.   With other salts, the order of adsorption varies with concentration.   The negative adsorption of alkali haloids by wood charcoal has been measured.[80]

The simultaneous adsorption of solvent and solute has been examined [81] in the system benzene–iodine–charcoal.   Equilibrium was attained through the vapour phase, and the temperature of the charcoal was kept above that of the liquid.   The adsorption of benzene from iodine solutions was less than that from pure solvent. A comparison of the adsorption of water and alcohol by charcoal [82] showed that the alcohol is adsorbed to nearly five times the extent of water.   The result is not in agreement with Langmuir's opinion [83] that equal volumes should be adsorbed.

Osmosis.

An equation for the osmotic pressure of mixtures has been deduced.[84]   The freezing-point depressions of pairs of non-electrolytes in concentrated solutions were determined separately and in admixture.   The osmotic pressure of the mixture may be less or greater than the sum of the partial osmotic pressures.   The facts are explained by van der Waals's theory of binary mixtures.

Donnan's theory of membrane equilibrium [85] has been applied [86] to the colloidal behaviour of proteins.   Gelatin chloride solutions (P_H 3·5) containing various concentrations of sodium nitrate, in collodion bags, were placed in aqueous hydrochloric acid (P_H 3·0) containing similar concentrations of sodium nitrate.   With increasing concentrations of neutral salt, the potential difference between the two solutions was depressed in the same proportion as the osmotic pressure of the gelatin chloride solution.   The potential

[79] S. Odén and H. Andersson, *J. Physical Chem.*, 1921, **25**, 311, *A.*, ii, 438; S. Odén and E. W. Langelius, *ibid.*, 385; *A.*, ii, 625.

[80] A. Pickles, *T.*, 1921, **119**, 1278.

[81] A. M. Bakr and J. E. King, *ibid.*, 454.

[82] J. Driver and J. B. Firth, *ibid.*, 1126.

[83] *J. Amer. Chem. Soc.*, 1917, **39**, 1848.

[84] R. Cernatesco, *Ann. Sci. Univ. Jassy*, 1920, **10**, 259; *Chem. Zentr.*, 1921, iii, 199; *A.*, ii, 576.

[85] *Z. Elektrochem.*, 1911, **17**, 572; *A.*, 1911, ii, 848; *T.*, 1911, **99**, 1554; 1919, **115**, 1313.

[86] J. Loeb, *J. Gen. Physiol.*, 1921, **3**, 557, 667, 691; *A.*, i, 368, 627; compare *A.*, 1920, ii, 14, 234, 358, 476, 477, 602.

differences agreed with those calculated by Nernst's formula on the assumption that they were due to P_{H}. The effect of salts on the swelling or viscosity of gelatin chloride is similar. The results are explained by an unequal distribution of non-colloid ions on the two sides of the membrane. Proctor's expression [87] for the Donnan equilibrium is verified. Electro-osmose in liquids of low conductivity has been studied [88] by driving a liquid through a capillary tube and measuring the $E.M.F.$ A proportionality was found to exist between the $E.M.F.$ and the external pressure, as required by theory. A marked increase in the conductivity of a badly conducting liquid raises the potential difference at the surface of contact with the solid.

J. R. PARTINGTON.

[87] *T.*, 1914, **105**, 313; 1916, **109**, 307.
[88] W. Staszewski, *Krakau Anzeiger*, 1917, [*A*], 269; *Chem. Zentr.*, 1920; iii, 782; *A.*, ii, 13.

INORGANIC CHEMISTRY.

A GENERAL survey of the progress made during the year 1921 shows that whilst no new discovery of transcendent interest has been made, the great advances achieved in 1920 have been consolidated, and indeed in some cases have been still further extended. To those who keep pace with the rapid progress into virgin country by such pioneers as Rutherford, chemistry as she is to-day must present a fascination that never before was theirs. The reporter well remembers Sir Ernest saying that the mystery of the positive atomic nucleus by common consent must be left to a future generation to solve. By his newest work, however, he has already poached on the preserves of posterity, since a proof of the existence of H nuclei as satellites of a central nucleus would go far towards an elucidation of this mystery.

Apart from its bearing on Bohr's theory and the emission of spectra, this work leads to the conclusion that the atomic masses of the elements are not all exact whole numbers, as Aston's work has suggested. In the case of the elements with atomic masses given by $4N + 2$ and $4N + 3$, these atomic masses would be greater than whole numbers by 2×0.008 and 3×0.008, respectively, owing to the fact that the two or three H nuclei are satellites of the inner nucleus and do not form an integral part of a closely-packed nucleus.

In view of the fact that a large number of the elements as we know them are mixtures of two or more isotopes, it is a very remarkable fact that the experimentally determined atomic weights should be constant. It has even been found that the atomic weights of terrestrial nickel and of nickel found in meteorites only differ by an amount that lies within the limit of experimental error, in spite of the fact that this element is a mixture of two isotopes in the ratio of $2 : 1$. It is necessary to believe that in the genesis of this element, and indeed of all " impure " elements, the isotopes were always produced at the same time, at the same rate, and in the same place. The genetic processes of the isotopes of any one element must therefore have been closely connected so that one could not occur without the other, the products always being formed in constant ratio which probably was independent of

temperature and pressure, for it is impossible to believe that all the nickel which has yet been experimented with was formed under identical conditions of temperature and pressure.

Apart from this work on atomic theory and structure, there is much of great interest to be recorded on more stereotyped lines. Indeed, it may be said that the year's work is of great interest to all students of inorganic chemistry.

Atomic Theory.

Sir Ernest Rutherford has extended his investigations of the artificial disintegration of the light elements and has been able to draw certain conclusions, one of which would seem to be of very great importance.[1] It will be remembered that when the swiftly moving α-particles from radium-C pass through dry air or nitrogen, a few long-range particles are formed which can be detected by their scintillations on a zinc sulphide screen. These particles are bent in a magnetic field to about the same extent as swift H atoms of the same range, and there is little doubt that some of the nitrogen atoms are disintegrated by the intense collisions with the α-particles and that positively charged H atoms are liberated at a high speed. No such long-range particles are observed in oxygen or carbon dioxide. By improvements in the observing microscope, the counting of the scintillations has been made much easier and more certain. It has now been found that the particles from nitrogen have a much greater range of penetration than the corresponding H atoms from hydrogen. For example, using radium-C as a source of α-rays with a range in air of 7 cm., no H atoms from hydrogen can be detected after passing through screens of aluminium or mica of stopping power equivalent to 29 cm. of air. On the other hand, the maximum range of the particles from nitrogen corresponds with 40 cm. of air. This proves that these particles cannot be due to the presence of free hydrogen or hydrogen compounds, and also enables other elements besides nitrogen to be tested. If the scintillations are counted for absorptions greater than 29 cm. of air, the results are independent of the presence of hydrogen as an impurity.

The following table contains in the first column a list of the elements examined. The second column contains the materials actually used, the third column gives the number of scintillations observed per minute per milligram activity of the source at an absorption of 32 cm. of air, and the fourth column the maximum range of the particles:

[1] (Sir) E. Rutherford and J. Chadwick, *Phil. Mag.*, 1921, [vi], **42**, 809; *A.*, ii, 671.

Element.	Material.	No. of particles per min. per mg.	Maximum range of particles in cm. of air.
Lithium	Li_2O	—	—
Glucinum	GlO	—	—
Boron	B	0·15	ca. 45
Carbon	CO_2	—	—
Nitrogen	Air	0·7	40
Oxygen	O_2	—	—
Fluorine	CaF_2	0·4	over 40
Sodium	Na_2O	0·2	ca. 42
Magnesium	MgO	—	—
Aluminium	Al, Al_2O_3	1·1	90
Silicon	Si	—	—
Phosphorus	P (red)	0·7	ca. 65
Sulphur	S, SO_2	—	—

In addition to these, the following were examined—chlorine as $MgCl_2$, potassium as KCl, calcium as CaO, titanium as Ti_2O_3, manganese as MnO_2, iron, copper, tin, silver, and gold in the form of metal foils. In no case were any particles observed of range greater than 32 cm. of air.

The effect of using α-particles of different velocities was investigated, the different ranges being 8·6, 7·0, 6·0, and 4·9 cm., respectively. The very interesting and important result was obtained that with a given element the particles observed increase rapidly in number and in velocity with the velocity of the α-particles.

It is reasonable to expect that the great majority of particles liberated from the various elements would be expelled in the direction of the α-particles, but in the case of aluminium it was found that the direction of escape is to a large extent independent of the direction of the α-particles. Nearly as many are expelled in the backward as in the forward direction, but the velocity in the backward is less than that in the forward direction.

There is little doubt that the particles are in all cases H atoms, which are released at different maximum speeds depending on the element and on the velocity of the incident α-particle. Of those so far examined, only those with atomic weights given by $4n + 2$ or $4n + 3$, where n is a whole number, give rise to H atoms. Elements of mass $4n$ like carbon, oxygen, and sulphur show no effect. This is clearly shown in the following table of elements which give H atoms :

Element.	Mass.	$4n + a$.
Boron	11	$2 \times 4 + 3$
Nitrogen	14	$3 \times 4 + 2$
Fluorine	19	$4 \times 4 + 3$
Sodium	23	$5 \times 4 + 3$
Aluminium	27	$6 \times 4 + 3$
Phosphorus	31	$7 \times 4 + 3$

This result receives a simple explanation on the assumption that the nuclei of these elements are built up of helium nuclei of mass

4 and of hydrogen nuclei. The importance of the helium nucleus as a unit of atomic structure in the heavy elements has been established by the study of radioactive changes. In order to account for the liberation of an H atom at high speed, it is natural to suppose that the H nuclei are satellites of the main nucleus. In a, close collision, the α-particle is able to give sufficient energy to the satellite to cause its escape at high speed from the nucleus. The escape of the H atoms in all directions is readily explained on this supposition, since the directions will be determined by the angle at which the α-particles strike the orbit of the satellite. If the direction of the α-particles is tangential to the orbit, the H atom will be driven in the forward direction of the α-particles and away from the nucleus. If the H atom is driven towards the nucleus, it will describe an orbit close to the nucleus and escape in a backward direction. The difference in the velocity of the H atoms in the forward and backward directions is probably due to the fact that the nucleus has been set in motion in the direction of the α-particles before the close collision with the H satellite occurs. On this view, the relative velocity of the H atom and the residual nucleus is the same whether the H atom escapes in the backward or forward direction, but the actual velocity in the backward direction is less.

In the case of aluminium the law of conservation of energy does not hold unless the energy derived from the disintegration of the nucleus is taken into account. By making the three assumptions that the law of conservation of momentum is valid, that the resultant kinetic energy of the three bodies involved is the same whether the H atom is liberated in the forward or backward direction, and that the final energy of escape of the α-particle is not sensibly different in the two cases, it is possible to calculate the final distribution of energy between the three bodies involved. In the case of an α-particle with range of 7 cm., it is found that the total gain of energy of the parts after a collision is 0·45 × the energy of the incident α-particle.

If the view is correct that the H nuclei are satellites of the central nucleus, the mass of the H satellite should not be very different from that of the free H nucleus, since the packing effect is absent. On the assumption that $C = 12·00$ and $H = 1·008$, the true atomic weight of nitrogen should be $12 + 2 \times 1·008 = 14·016$. Similar considerations should be applicable to the other elements from which H atoms can be liberated.

Reference must be made to some further work by Dr. Aston on the mass spectra of the elements.[2] The general method of the

[2] *Phil. Mag.*, 1920, [vi], **40**, 628; [vi], **42**, 140, 436; *A.*, 1920, ii, 718; 1921, ii, 474, 565. *Nature*, 1921, **107**, 520. *T.*, 1921, **119**, 677.

investigation was described in the Report for last year and it is only necessary to record the new results that have been obtained. Boron is a mixture of two isotopes of masses 10 and 11, the second of which is present in greater amount. The relative amounts of the two present, however, do not seem to agree well with an observed atomic weight as high as 10·9, but no evidence was found of the existence of an isotope with mass 12. Whilst fluorine was found to be a simple element, silicon consists of two isotopes 28 and 29, but the relative amounts of these two would give an atomic weight less than 28·3, and therefore in spite of the complete absence of experimental evidence there may be a third isotope of mass 30.

Bromine is an interesting case, because, instead of being almost a pure element of mass 80, it consists of an almost equal mixture of two isotopes with masses 79 and 81. Phosphorus and arsenic are both simple elements, and the experimental evidence is in favour of this also being the case with sulphur, in spite of the fact of the accepted value of the atomic weight.

The essential condition for satisfactory measurement of the atomic masses with the positive ray spectrograph is, of course, the existence of stable volatile substances which may either be the elements themselves or their compounds with other elements of known atomic mass. The majority of the elements do not satisfy this condition, and consequently, as elements less and less suitable are examined, the work becomes more difficult and the results either inconclusive or entirely negative. Thus no satisfactory measurements have as yet been made with selenium, tellurium, antimony, and tin. Iodine, on the other hand, which was used in the form of methyl iodide, gave very decided evidence of being a simple element of mass 127. As Dr. Aston says, this result is unexpected, since all the speculative theories of atomic evolution predict a complex iodine; thus Kohlweiler deduces five isotopes of masses 122, 124, 126, 128, and 130, and he also claims to have achieved a considerable separation of these by diffusion.

The earlier results obtained with xenon and chlorine have been revised. A purer specimen of xenon showed definite evidences of five isotopes of masses 129, 131, 132, 134, and 136, with distinct indications of a sixth component, 128, present in smaller quantity. It is possible also that there is a seventh isotope of mass 130. In the case of chlorine, strong confirmatory evidence has been obtained of the definite existence of the two isotopes 35 and 37, but the question of the third with mass 39 still remains in doubt.

It has been found possible by the use of an anode which was electrically heated by the current from a storage battery to observe the mass spectra of the alkali metals. In each case the anode was

coated with the salt of the metal. It was found that lithium is a mixture of two isotopes of masses 6 and 7, that sodium is a single element, that potassium and rubidium are mixtures of two isotopes, 39, 41, and 85, 87 respectively, and that cæsium is a single element of mass 133. The atomic weight of cæsium, 132·81, suggests the presence of a lighter isotope, but no evidence of this could be found, and if it exists it must be in very small amount.

Finally, by the use of nickel carbonyl, it has been found that nickel consists of two isotopes of masses 58 and 60 in the proportion of 2 : 1. This gives a value for the atomic weight of 58·67, which agrees closely with the accepted value. The whole of the observations may be tabulated as follows, the doubtful isotopes being enclosed within brackets.

Element.	Atomic number.	Atomic weight.	Minimum no. of isotopes.	Masses of isotopes in order of intensity.
H	1	1·008	1	1·008
He	2	3·99	1	4
Li	3	6·94	2	7, 6
B.	5	10·9	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22, (21)
Na	11	23·00	1	23
Si	14	28·3	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37, (39)
A	18	39·88	(2)	40, (36)
K	19	39·10	2	39, 41
As	33	74·96	1	75
Br	35	79·92	2	79, 81
Kr	36	82·92	5	84, 86, 82, 83, 80, 75
Rb	37	85·45	2	85, 87
I	53	126·92	1	127
X	54	130·2	5 (7)	129, 132, 131, 134, 136, (128), (130 ?)
Cs	55	132·81	1	133
Hg	80	200·6	(6)	(197–200), 202, 204

Mention may also be made of measurements with a heated magnesium anode which establish the existence of three isotopes of masses 24, 25, and 26, which occur in the proportion of 6 : 1 : 1 and give an average atomic weight of 24·375.[3]

An interesting positive result in the partial separation of the isotopes of mercury has been announced.[4] Two methods were employed, namely, evaporation and effusion. The density difference between the lightest and heaviest mercury was 0·49 per cent.,

[3] A. J. Dempster, *Science*, 1920, **52**, 559; *A.*, ii, 402.
[4] J. N. Brønsted and G. Hevesy, *Phil. Mag.*, 1922, [vi], **43**, 31.

which corresponds with a difference of 0·1 in the atomic weight of the element. The results of the experiments agree with the theory that the evaporation rate and effusion rate of the isotopes are inversely proportional to the square root of their molecular masses. Moreover, they conform with Aston's determinations of the atomic masses of the isotopes.

Atomic Weights.

Several papers have been published on the determination of atomic weights since the writing of the last Report. Of these, the following may be referred to.

Aluminium.—Aluminium bromide was synthesised from very pure bromine and the purest obtainable aluminium.[5] It was digested three times in nitrogen at different temperatures, and fractionated by distillation twice in nitrogen and twice in a vacuum. The bromide was decomposed by water in such a way that the reaction occurred slowly, and the solution was precipitated by a weighed amount of pure silver. The silver bromide was collected and weighed. From the result of four closely agreeing analyses, the atomic weight was found to be 26·963. The modern evidence seems to show that the atomic weight of aluminium is really less, not more, than 27. The new value is distinctly nearer to a whole number than the old one.

Antimony.—Three preparations of antimony were combined with bromine,[6] the resulting product was twice distilled under a pressure of 5—10 mm. as long as gaseous materials could be removed, and then distilled a third time under a pressure of less than 1 mm. into a series of small bulbs, which were sealed off as filled. The product was analysed for bromine in two ways; first, by finding the amount of silver equivalent to the sample in the usual way, secondly, by adding excess of silver nitrate, filtering, and weighing the silver bromide. Averaging the volumetric result for eleven samples with the gravimetric results for eight samples, the most probable atomic weight for antimony becomes 121·773.

Bismuth.—Bismuth triphenyl was prepared by the action of an excess of bismuth bromide on magnesium phenyl bromide.[7] The product was decomposed by ice-water and distilled in a current of steam. The bismuth triphenyl was purified by crystallisation from absolute alcohol, and distillation, and for the purpose of atomic weight determination was left for ten hours over phosphoric oxide

[5] T. W. Richards and H. Krepelka, *J. Amer. Chem. Soc.*, 1920, **42**, 2221; *A.*, ii, 48.

[6] H. H. Willard and R. K. McAlpine, *ibid.*, 1921, **43**, 797; *A.*, ii, 405.

[7] A. Classen and O. Ney, *Ber.*, 1920, **53**, [*B*], 2267; *A.*, ii, 119.

in a cathode-ray vacuum before weighing. It was converted into bismuth oxide by mixing weighed portions with pure oxalic acid in a porcelain crucible, moistening with pure alcohol, heating in an electric quartz muffle furnace, and finally ignited in a stream of oxygen. From ten determinations, the mean atomic weight was · found to be 208·9967.

Reference was made in last year's Report to Hönigschmid's work, and a detailed account of this work has since been published.[8] Two series of analyses of bismuth chloride and bismuth bromide are recorded. In each series, the atomic weight was determined by two independent methods, gravimetric estimation of the ratios $BiCl_3 : 3AgCl$ and $BiBr_3 : 3AgBr$, and nephelometric measurement of the silver haloid dissolved in the mother-liquor, and determination of the ratios $BiCl_3 : 3Ag$ and $BiBr_3 : 3Ag$ by gravimetric titration with the aid of the nephelometer. The mean value of the six most trustworthy series is $Bi = 208·997$ or in round numbers 209·00.

Classen and Ney's value has been re-calculated with the result that $Bi = 208·91$ which is 0·09 lower. Both values are decidedly higher than the international value.

Cadmium.—The atomic weight of cadmium has been re-determined by the electrolysis of anhydrous cadmium sulphate,[9] it having been found that the hydrated salt generally contains a small amount of water above that required for the composition $CdSO_4,8/3H_2O$, and since such water cannot be removed, the hydrated salt is unsuitable for atomic weight determination. The weighed sulphate was dissolved in water and electrolysed, a weighed mercury cathode being used. As the result of eleven analyses, the value 112·409 was obtained for the atomic weight. The mean of the whole of the work of Baxter and his collaborators on the atomic weight of cadmium is 112·411.

Germanium.—The method employed was the conversion of potassium germanofluoride into potassium chloride by heating in hydrogen chloride.[10] Very great care was taken in the purification of the germanium compounds before the double salt was prepared. The mean of seven determinations gave $Ge = 72·418$.

Lanthanum.—Two samples of lanthanum material were subjected to a prolonged series of crystallisations as double ammonium lanthanum nitrate, and the material finally obtained was shown to be entirely free from the other rare earths by spectroscopic examina-

[8] O. Hönigschmid and L. Birckenbach, *Ber.*, 1921, **54**, [*B*], 1873; *A.*, ii, 646.

[9] G. P. Baxter and C. H. Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 1230; *A.*, ii, 640.

[10] J. H. Müller, *ibid.*, 1085; *A.*, ii, 456.

tion.[11] From six determinations, the ratio $LaCl_3 : 3Ag$ was found to give the atomic weight of 138·914. Seven determinations of the ratio $LaCl_3 : 3AgCl$ gave the atomic weight as 138·912. This is lower than the accepted value, 139·0, but since the presence of the usual companions of lanthanum, cerium, praseodymium, and neodymium, would raise the apparent atomic weight, this value must be regarded as a maximum.

Tellurium.—Pure tellurium dioxide was dissolved in pure aqueous sodium hydroxide and the tellurium estimated volumetrically either in alkaline or just acid solution.[12] The mean of twelve estimations in alkaline solution gave the value 127·8 for the atomic weight, and of nine estimations in acid solution the value 127·65.

Thulium.—The atomic weight of thulium has been determined from the ratio $TmCl_3 : 3Ag$ from three specimens of thulium.[13] The purest fraction gave a value 169·44 for the atomic weight as a mean of three determinations, whilst the other two fractions, which contained neoytterbium, gave 169·66 and 169·90, respectively.

Zinc.—The atomic weight of zinc has been re-determined by means of the electrolytic estimation of the amount of zinc in zinc chloride.[14] The carefully purified metal was converted into the bromide, and the purified salt fused in a current of chlorine. As a mean of eleven analyses of the chloride the value 65·372 was obtained, or, rejecting four relatively low values, 65·379. This value is in good agreement with recent determinations and indicates that the true atomic weight lies very close to 65·38.

Nickel.—A comparison has been made of the atomic weights of terrestrial and meteoric nickel, the method employed being the reduction of nickelous oxide with hydrogen.[15] As a result of nine determinations with terrestrial material, a mean value of 58·70 was found, whilst three experiments with meteoric nickel gave 58·68. The difference is considered to be within the limits of experimental error.

Catalysis.

Yet another theory has been added to the list of those which have been put forward to explain the rusting of iron.[16] According to this theory, iron is passive towards distilled water in the absence

[11] G. P. Baxter, M. Tani, and H. C. Chapin, *J. Amer Chem. Soc.*, 1921, **43**, 1080; *A.*, ii, 454.

[12] P. Bruylants and G. Desmet, *Bull. Soc. chim. Belg.*, 1914, **28**, 264; *A.*, ii, 448.

[13] C. James and O. J. Stewart, *J. Amer. Chem. Soc.*, 1920, **42**, 2022; *A.*, 1920, ii, 759.

[14] G. P. Baxter and J. H. Hodges, *ibid.*, 1921, **43**, 1242; *A.*, ii, 639.

[15] G. P. Baxter and L. W. Parsons, *ibid.*, 507; *A.*, ii, 338.

[16] J. A. N. Friend, *T.*, 1921, **119**, 932.

of a catalyst and passes into solution, but only with extreme slowness, owing to the traces of electrolytes that are present. The iron passes into solution as ferrous ions, but is rapidly converted into the sol of ferrous hydroxide. This sol is oxidised by the dissolved oxygen to the sol of a higher hydroxide, which now acts catalytically, by oxidising metallic iron with relatively great rapidity and simultaneously being reduced to the lower hydroxide, only to be oxidised again by the dissolved oxygen. In other words, the sol acts as an oxygen carrier.

A number of experimental results are given in support of this theory. In the first place, if pure metallic iron is suspended in a stream of water, the amount of corrosion increases to a maximum as the velocity of the stream is increased. With further increase in the velocity of the water, the amount of corrosion decreases to a minimum. There was, however, a distinct loss in weight of the iron even when the velocity was 30,000 feet an hour, but this is attributed to mechanical erosion. Somewhat analogous observations were made of the potential difference between iron and platinum wires immersed in dilute solutions of electrolytes at rest and in motion. Slight movement increases the potential difference, but a maximum is soon attained, after which an increase in velocity causes the potential difference to fall to a constant value. These results are interpreted to mean that the rapidly moving water sweeps away the colloid from the surface of the iron.

If the suggested theory is correct, then the inhibiting effect of dissolved salts on the corrosion of iron should be proportional to the coagulating power of the salts on hydrosols. Some measurements of the effect of solutions of certain salts on corrosion show decreases which are comparable with their precipitating powers towards colloidal ferric hydroxide. Confirmatory evidence is also found in the inhibiting action on the corrosion of protective colloids, of colloid poisons, and of the β- and γ-rays from radium.

It is further suggested that this theory is of more general application, since many reactions which have hitherto been ascribed to ions may possibly be explained more readily on the autocolloid, catalytic theory. Many so-called catalysts, which are known to be chemically inert, may act by rendering possible the existence of a colloid catalyst formed from the reacting substances themselves. They are not, therefore, true catalysts in the sense of actually taking part in the reactions themselves, but may be termed secondary catalysts. For instance, the addition of dry benzene causes instant combination between perfectly pure and dry ammonia and hydrogen chloride. It is quite in accord with the behaviour of benzene, however, to suppose that it facilitates the formation and stabilisation

of a colloidal form of ammonium chloride, which catalytically assists the union of the remaining ammonia and hydrogen chloride.

Whilst not necessarily denying the correctness of Dr. Friend's theory of the corrosion of iron, the reporter feels that his proposed application to such cases as ammonia and hydrogen chloride is open to criticism, mainly for the reason that it offers no explanation. The statement that the known catalytic effect of benzene on a mixture of ammonia and hydrogen chloride is due to the fact that it forms another catalyst does not advance our knowledge. The essential underlying factor in all reaction is energy, and the rôle of the catalyst is to supply the necessary energy to the catalyte. Every reaction consists of three stages, and the first of these is the conversion of the reactant molecules from their normal and non-reactive phase into the reactive phase, a change which requires the supply of energy to the molecules. The second stage is the re-arrangement of the atoms whereby new compounds are produced, and it is this stage, and this stage only, which is expressed by the chemical change of the reaction. The third stage is the conversion of the newly synthesised molecules into their normal and non-reactive phase. The second and third stages are accompanied by an evolution of energy, and the observed heat of the reaction is the difference between the sum of the two amounts of energy evolved in the second and third stages and that absorbed in the first stage.

The energy necessary for the first stage may be gained by ex-posing the reactant molecules to heat or light, when the reaction is called thermal or photochemical. The necessary increment of energy may also be supplied by a material catalyst, the word catalyst being used in the broadest sense. In whatever way the catalyst behaves, the fact remains that it functions as a supplier of energy to the reactant molecules, whereby they are converted from the non-reactive to the reactive phase.

It is true that many reactions may be said to proceed without the addition of a specific catalyst, but this is simply due to the fact that the reactant molecules have already been brought into their reactive phases by the use of a solvent, the solvent, of course, being the catalyst. Then, again, there is the phenomenon of autocatalysis, when the velocity of a reaction, at first small, increases up to a maximum. When the second and third phases of the reaction are taking place, energy is radiated, and this energy can be re-absorbed by the surrounding reactant molecules, with the result that more of these are activated and the velocity increases to a maximum defined by the amount of the radiated energy that is re-absorbed. This has been proved to take place in the case of the photochemical union of

hydrogen and chlorine, and in the photosynthesis of formaldehyde and sugars from carbon dioxide and water.

To take the case quoted of ammonia and hydrogen chloride, these gases, when pure and dry, exist in their non-reactive phases, and the catalyst, whether it be water vapour or benzene, supplies energy to the molecules so that they are converted into their re-active phases, which instantly combine to form ammonium chloride. The statement that one catalyst acts by producing another is of little use, for, if explanation is sought of the rise in velocity observed after the reaction has commenced, it is to be found in the re-absorption by the reactant molecules of the energy radiated in the reaction between a few of these.

It may be noted that the very interesting observation made by Sugden can be explained very readily on this theory.[17] The activity of nascent hydrogen is by no means necessarily due to its dissociation into free atoms. The normal, non-reactive hydrogen molecule can be rendered active for certain reactions by an amount of energy which is smaller than that required to dissociate it into atoms. This is exemplified by the activation of a portion of the hydrogen when three volumes of this gas are exploded with one volume of oxygen.[18] The residual gas reduces alkaline potassium permanganate to manganate, indigotin in alkaline solution to indigo-white, ferric chloride to ferrous chloride, potassium nitrate to potassium nitrite, arsenious acid to arsine, potassium perchlorate to potassium chloride, etc. A similar explanation is applicable to the active form of hypophosphorous acid.[19]

In their important paper on the catalytic oxidation of ferrous salts, Thomas and Williams [20] recognise that neither intermediate compound formation nor adsorption alone is capable of explaining catalysis. The key to the problem is the transference of energy to the catalyte by way of the intermediate compound or of adsorption. Again, in the cases of heterogeneous catalysis by metals, it follows from this theory that the activation by the catalyst cannot extend to more than a molecular layer of the catalyte. The experimental evidence supports this conclusion very strongly, and the particular case of palladium is dealt with under Group VIII.

In conclusion, two questions may be asked as regards Dr. Friend's theory of the corrosion of iron, which in spite of their very obvious nature do not seem to have been dealt with in his paper. The first of these is, Why is rust formed and not a solution of ferric

[17] S. Sugden, *T.*, 1921, **119**, 233.
[18] Y. Venkatramaiah, *Nature*, 1920, **106**, 46.
[19] A. D. Mitchell, *T.*, 1921, **119**, 1266.
[20] R. Thomas and E. T. Williams, *ibid.*, 749.

hydroxide sol? The second question is, Does iron rust with greater rapidity in a solution of ferric hydroxide sol?

Group I.

The properties of pure hydrogen peroxide have been investigated and a method given for its preparation.[21] Three per cent. hydrogen peroxide, obtained from barium peroxide, is concentrated to 30 per cent. by means of a sulphuric acid concentrator.[22] It is then distilled at very low pressure to remove the non-volatile impurities. A further concentration by the sulphuric acid concentrator at 0° raises the concentration to 90 per cent., and the final product, 100 per cent. hydrogen peroxide, is obtained by fractional solidification and melting. The pure substance is found to have the following physical properties : m. p. $-1.70°$, density of liquid at $-0.53°$ 1.4638, association factor 3.48, specific heat between 0° and $18.5°$ 0.5730, latent heat of fusion 73.91 cal. Hydrogen peroxide is very slightly soluble in ether, it dissolves many normal salts, and it attacks glass. Freezing-point determinations of solutions of hydrogen peroxide in water show that only one compound, $H_2O_2, 2H_2O$, exists with melting point $-51°$.[23]

Some work has been done on the hydrides of the alkali metals. In the case of lithium hydride, it would seem that the substance possesses the properties of a salt.[24] Electrolysis of the compound gives lithium at the cathode and, apparently, hydrogen at the anode, this being the first observed instance of hydrogen functioning as a negatively charged ion. The following constants were determined : density 0.816, molecular volume 9.77, heat of formation $21,600 \pm 250$ cal., $Li + H_2O = LiOH + H + 52,723 \pm 200$ cal., $LiH + H_2O = LiOH + H_2 + 31,110 \pm 50$ cal.

Pure sodium hydride can best be prepared by leading a rapid stream of hydrogen directly on to the surface of the metal at such a temperature that a yellow glow is produced.[25] The temperature must be above 350°, when the sodium hydride is carried away as a white smoke, which is precipitated electrically and filtered through glass wool. Potassium hydride can be obtained by leading the gas into the metal at 350°. The reaction in each case is facilitated by the presence of metallic calcium.

Rubidium and cæsium hydrides were prepared by heating a

[21] O. Maass and W. H. Hatcher, *J. Amer. Chem. Soc.*, 1920, **42**, 2548; *A.*, ii, 106.

[22] O. Maass, *ibid.*, 2571; *A.*, ii, 104.

[23] O. Maass and O. W. Herzberg, *ibid.*, 2569; *A.*, ii, 106.

[24] K. Moers, *Z. anorg. Chem.*, 1920, **113**, 179; *A.*, ii, 200.

[25] F. Ephraim and E. Michel, *Helv. Chim. Acta*, 1921, **4**, 762; *A.*, ii, 638.

mixture of their carbonates with metallic magnesium in hydrogen at 650° for five days and at 580—620° for three days, respectively. The stability of these hydrides decreases from sodium to cæsium.

Some doubt has been thrown on the correctness of the formula $NaBO_3,4H_2O$ for sodium perborate, it being stated that the composition is more correctly represented by $NaBO_2,H_2O_2,3H_2O$.[26] The salt, after partial dehydration at 50—55°, loses more water at 120° in a vacuum and the residue consists chiefly of $(NaBO_2)_2O_2$. This substance loses oxygen on treatment with water and has properties which differ from those of $NaBO_3$, and it is concluded that a substitution product of H_2O_2 exists with constitution

$$ONa{\cdot}B{<}{\overset{O}{\underset{O}{|}}}.$$
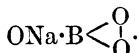
Three crystalline hydrates of disodium hydrogen phosphate are known with $12H_2O$, $7H_2O$, and $2H_2O$, respectively. The dihydrate can readily be prepared by boiling the finely-powdered dodecahydrate with ethyl alcohol, whilst the heptahydrate can be obtained by fusing the appropriate mixture of the dodecahydrate and dihydrate and cooling.[27] The following transition temperatures have been determined: $Na_2HPO_4,2H_2O$ — Na_2HPO_4, 94·97°; $Na_2HPO_4,7H_2O$ — $Na_2HPO_4,2H_2O$, 48·09°; $Na_2HPO_4,12H_2O$ — $Na_2HPO_4,7H_2O$, 35·0°. In addition to this, sharp breaks were observed in the heating and cooling curves for the dodecahydrate at 29·6°, due to a change of phase in this substance. Two forms of $Na_2HPO_4,12H_2O$ exist, of which one is stable between 29·6° and 35·0° and the other is stable below 29·6°. The existence of these two forms has been confirmed by solubility measurements.

It has been recorded that by the action of dry nitrogen peroxide on pure copper powder the compound Cu_2NO_2 is produced. Some further work has now been carried out on this reaction, as the result of which it has been proved that this compound does not exist.[28] The copper powder was prepared by reduction of copper oxide with hydrogen and by reduction of hydrated cuprous oxide with carbon monoxide. The cuprous oxide was obtained by pouring a solution of pure cuprous chloride in dilute hydrochloric acid into a dilute solution of sodium hydroxide. The product, after being dried over phosphoric oxide in a vacuum, was found to be $4Cu_2O,H_2O$.

When the copper powder was allowed to remain in contact with nitrogen peroxide, absorption took place, but no stoicheiometric relation could be found between the weight of the copper and the

[26] F. Foerster, *Z. angew. Chem.*, 1921, **34**, 354; *A.*, ii, 506.

[27] D. L. Hammick, A. K. Goadby, and H. Booth, *T.*, 1921, **119**, 1589.

[28] H. V. Tartar and W. L. Semon, *J. Amer. Chem. Soc.*, 1921, **43**, 494; *A.*, ii, 336.

increase in weight. Analysis of the product showed that the atomic ratio of nitrogen to oxygen was 1 : 3. Moreover, the product loses weight on being exposed to air due to the evolution of nitric oxide or nitrogen peroxide. When the product is treated with water, 90 per cent. of the nitrogen is found in the form of nitrate and 10 per cent. as nitrite. It is suggested that the reaction consists in the formation of anhydrous cuprous nitrate on the surface of the copper.

Group II.

A description has been given of the preparation of the yellow higher oxides of calcium and barium, and it is believed that these are the tetroxides.[29] The calcium compound may be prepared by gently warming calcium peroxide octahydrate with five to six times its weight of pure hydrogen peroxide (30 per cent.) until a vigorous evolution of oxygen occurs. The mixture is allowed to cool until the evolution of gas subsides, and the warming and cooling are repeated until practically no more gas is evolved. The precipitate is washed successively with water, alcohol, and ether, and dried. The product has a bright yellow colour and can be heated at 130° without change. It dissolves in acid with a brisk evolution of oxygen mixed with a small amount of carbon dioxide and with the formation of hydrogen peroxide. The evolved oxygen is inactive, since bromine is not liberated when the evolution takes place in an acidified solution of potassium bromide. The only known types of substance which evolve inactive oxygen are the oxyhydroxides, for example, $(KOH)_2O_2$, and the tetroxides, for example, K_2O_4. The stability of the calcium oxide towards heat excludes the first, so that in all probability it is calcium tetroxide, CaO_4. As judged by the amount of oxygen evolved, this substance is present to the extent of 8·7 per cent.

Barium tetroxide is much less stable than the calcium compound. The substance BaO_2,H_2O_2 can only be preserved for a short time at temperatures below 0°. At the atmospheric temperature, it rapidly becomes yellow owing to the formation of the tetroxide, and the colour increases in intensity during twenty-four to thirty-six hours, after which it disappears almost completely within four or five days, the complete reaction being $2BaO_2,H_2O_2 = 2BaO_2,H_2O + O_2$. If the highly coloured preparations are dissolved in acid, inactive oxygen is evolved corresponding in amount with about 8 per cent. of barium tetroxide in the best preparations. It was found impossible to prepare purer specimens of the tetroxides owing to the readiness with which the products decomposed in the presence of water.

[29] W. Traube and W. Schulze, *Ber.*, 1921, **54**, [B], 1626; *A.*, ii; 548.

Some work has been carried out on the crystallisation of calcium and magnesium carbonates with the view of explaining the natural formation of these salts and of dolomite.[30] In the presence of magnesium sulphate, calcium carbonate crystallises at 20° from water saturated with carbon dioxide only in the form of aragonite; 0·9 per cent. of magnesium sulphate is sufficient to inhibit the appearance of calcite. It was stated by Vaubel [31] that aragonite and calcite differ in that the former contains traces of a basic carbonate, but this has now been shown experimentally to be incorrect.

Saturated solutions of magnesium hydrogen carbonate deposit between 65° and the boiling point a basic carbonate, $4MgO,3CO_2,6H_2O$, in the form of slender needles. Between 65° and 55°, the basic carbonate separates, mixed with the trihydrate, $MgCO_3,3H_2O$; below 55°, the trihydrate alone is formed down to about 6°, and at 2° the unstable pentahydrate is formed.[32] All attempts to crystallise magnesite fail, and it is concluded that this mineral is of marine origin.

Numerous attempts were made to obtain synthetic dolomite by crystallisation of calcium and magnesium carbonates under different conditions, but without success. It is suggested that mixtures of the composition of dolomite are formed from sea-water, the mechanism of the recrystallisation as dolomite being unknown.

Various methods for the purification of mercury which has become contaminated with other metals by use in the laboratory have been suggested from time to time. It has been shown that distillation alone is not effective, and the treatment with nitric acid or mercurous nitrate solution is often of very little use. It is now claimed [33] that the most efficient method is to heat the metal at 150° in a flask while passing a current of air through it by means of a glass tube extending about 1 cm. below the surface. After several hours, the metal is filtered from the scum and again treated by the same method. The process is repeated until no further scum forms, after which the filtered metal is distilled in a vacuum from an ordinary fractionating flask.

The purification of impure mercury by treatment with air is not in any way new, and the novelty consists in the heating at 150°. It may be pointed out that a very essential necessity in all methods involving the treatment with air is the complete absence of dust.

Two methods have been described for the preparation of mercuric azide in a form which is less sensitive than the ordinary form.[34]

[30] H. Leitmeier, *Jahrb. Min.*, 1916, *Beil. Bd.*, **40**, 655; *A.*, ii, 112.
[31] *J. pr. Chem.*, 1912, [ii], **86**, 366; *A.*, 1912, ii, 1180.
[32] H. Leitmeier, *Z. Kryst. Min.*, 1909, **47**, 104; *A.*, 1910, ii, 49.
[33] C. Harries, *Z. angew. Chem.*, 1921, **34**, 359; *A.*, ii, 552.
[34] A. Stettbacher, *Z. ges. Schiess-u. Sprengstoffw.*, 1920, **15**, 211; *A.*, ii, 48.

It appears that the sensitivity is greatly dependent on the crystalline form. Thus, by mixing concentrated solutions of sodium azide and mercuric nitrate, mercuric azide is precipitated as a powdery mass. The salt as thus prepared is even less sensitive than lead azide, but it is converted into the highly sensitive form by recrystallisation.

Crystalline compounds of mercurous oxide with ammonia and sulphur dioxide have been prepared by the action of sulphur dioxide on the precipitate obtained from mercuric chloride and excess of ammonia.[35] The precipitate dissolves and the compounds separate when the solutions are evaporated under reduced pressure. If sulphur dioxide is first added and then ammonia, the compounds $Hg(SO_3 \cdot NH_4)_2$ and $HgCl(SO_3 \cdot NH_4)$ are produced. Excess of ammonia gives the compounds $Hg \cdot SO_3 \cdot NH_3$ and $Hg(SO_3 \cdot NH_4)OH$. In the presence of large amounts of ammonium chloride the compound $NH_3Cl \cdot Hg \cdot SO_3 \cdot NH_4$ is formed, which is converted by potassium hydroxide into Hg_2O,SO_3,NH_3.

Group III.

Boron nitride has been prepared in quantity by leading a mixture of boron trichloride vapour and ammonia through an intensely heated tube.[36] Difficulty was caused by the voluminous nature of the nitride, but this was overcome by the use of a quartz tube which was electrically heated in zones. The yield was 80—85 per cent., and the nitride was obtained as a colourless powder, the reactivity of which depends on the temperature at which the reaction is carried out. At 800°, a very voluminous product is obtained which, after exposure to the atmosphere, gives some ammonia. The product obtained at much higher temperatures is more stable in air.

A convenient method has been given for the preparation of calcium arsenide which can be employed for the formation of hydrogen arsenide.[37] A neutral diluent such as sand or calcium arsenide from a previous preparation is added to the extent of 50 per cent. by weight to a mixture of powdered arsenic and calcium filings. The whole is placed inside a sheet-iron container enclosed within a second vessel. The reaction is started by means of a magnesium–potassium chlorate mixture and steadily proceeds throughout the entire mass. There is no flame and very little arsenious oxide is formed.

The resulting calcium arsenide, on treatment with water or acids,

[35] O. Ruff and E. Kröhnert, *Z. anorg. Chem.*, 1920, **114**, 203; *A.*, ii, 202.

[36] F. Meyer and R. Zappner, *Ber.*, 1921, **54**, [B], 560; *A.*, ii, 329.

[37] H. Thoms and L. Hess, *Ber. Deut. Pharm. Ges.*, 1920, **30**, 483; *A.*, ii, 110.

gives hydrogen arsenide containing 14 per cent. by volume of hydrogen. Aqueous solutions of the gas undergo rapid decomposition with formation of colloidal arsenic, and the reaction may be followed by titration with $N/100$-iodine solution. At first, the hydride is oxidised according to the equation $AsH_3 + 3I_2 + 3H_2O = H_3AsO_3 + 6HI$. After rendering the solution alkaline by the addition of potassium hydrogen carbonate, the normal oxidation to arsenic acid takes place.

An acid fluoride of thallium, H_2TlF_3, is obtained by dissolution of thallium in hot dilute hydrogen fluoride and evaporation of the solution to dryness.[38] The salt loses hydrogen fluoride on being heated and forms with water acid solutions, which, however, do not attack glass. The neutralisation curve shows that two types of complex salts exist, for example, $KHTlF_3$ and K_2TlF_3.

Group IV.

An important paper has appeared on the preparation of the trithiocarbonates and perthiocarbonates of the alkali and alkaline earth metals.[39] The general method of preparation was the addition of the requisite amount of carbon disulphide to alcoholic solutions of either the hydrosulphides or the disulphides of the metals. These solutions were obtained by the method described by Rule and Thomas. After the carbon disulphide had been added, the thiocarbonates separated after dilution with ether. The operations were carried out in an atmosphere of hydrogen, since the salts readily decompose in the presence of moist air or carbon dioxide. Sodium trithiocarbonate, Na_2CS_3,H_2O, forms very deliquescent needles with a pinkish-yellow colour. They give a distinctly red solution in water, which is stable if oxygen and carbon dioxide are rigidly excluded. The perthiocarbonate, $Na_2CS_4,3H_2O$, separates as brownish-yellow needles and is very deliquescent. It readily dissolves in water to a distinctly yellow solution. The heats of formation of sodium trithiocarbonate and sodium perthiocarbonate in alcoholic solution were found to be 5700 and 8550 cals., respectively.

The following salts were also prepared, K_2CS_3; $2K_2CS_4,H_2O$; $3Ca(OH)_2,CaCS_3,9H_2O$; $Ca(OH)_2,CaCS_3,2H_2O$; $2Ca(OH)_2,CaCS_4,8H_2O$; $SrCS_3,4H_2O$; $SrCS_4,8H_2O$; $BaCS_3$; $(NH_4)_2CS_3$; $(NH_4)_2CS_4$; $(NH_4)_2CS_4,H_2O$.

Reference may be made to some further work on the hydrides of silicon and their derivatives.[40] Attempts were made to synthesise

[38] Barlot, *Compt. rend.*, 1920, **171**, 1143; *A.*, ii, 113.

[39] E. W. Yeoman, *T.*, 1921, **119**, 38.

[40] A. Stock and K. Somieski, *Ber.*, 1921, **54**, [*B*], 524; *A.*, ii, 330.

disilane by the action of the alkali metals on monochlorosilane, but the results obtained were unexpected.

Monochlorosilane reacts readily with potassium at the ordinary temperature, but the metal becomes coated with a protective layer which speedily inhibits the reaction. At 300°, the reaction is complete, the products being silicon, potassium hydride, potassium chloride, and hydrogen. When allowed to remain in contact with potassium–sodium alloy for a month, monochlorosilane gave an incomplete reaction. The chief volatile product was monosilane, whilst disilane could only have been present in traces. When sodium amalgam was used, the chief product again was monosilane mixed with a small amount of hydrogen, but in this case the presence of disilane in small quantity was definitely established. Disilane undergoes slow decomposition in the presence of sodium–potassium alloy or of sodium amalgam to give hydrogen and monosilane. It may be noted that methyl chloride behaves similarly to monochlorosilane towards sodium amalgam, since it gives methane and ethane. Dichloromonosilane is converted by sodium amalgam into monosilane and hydrogen.

Chlorosilane and ammonia [41] react at the ordinary temperature quantitatively to give ammonium chloride and trimonosilylamine, $N(SiH_3)_3$. The latter is a spontaneously inflammable liquid with m. p. $-105 \cdot 6°$, b. p. $52°$, and density $0 \cdot 895$. It is stable in the absence of air and is vigorously decomposed by water according to the equation $N(SiH_3)_3 + 6H_2O = 3SiO_2 + NH_3 + 9H_2$. The vapour density corresponds with the simple formula, $N(SiH_3)_3$, and the substance does not combine with hydrogen chloride or monochlorosilane.

By the action of an excess of ammonia on monochlorosilane, the initial product obtained is chiefly dimonosilylamine, $NH(SiH_3)_2$, which is probably mixed with the corresponding tri- and mono-amines. The diamine is only comparatively stable and decomposes gradually according to the equation $NH(SiH_3)_2 = SiH_4 + SiH_2{:}NH$. The last compound cannot exist in the uni-molecular form and condenses rapidly to the solid polymeride, $(SiH_2{:}NH)_x$. A second reaction also takes place to a smaller extent with evolution of ammonia, $SiH_3 \cdot NH_2 \longrightarrow NH(SiH_3)_2 \longrightarrow N(SiH_3)_3$, with the result that the composition of the final residue corresponds with that of a mixture of $(SiH_2{:}NH)_x$ and $N(SiH_3)_3$.

Between dichlorosilane and excess of ammonia the following reaction takes place at the ordinary temperature, $SiH_2Cl_2 + 3NH_3 = 2NH_4Cl + SiH_2{:}NH$.

The polymeride, $(SiH_2{:}NH)_x$, is a white substance resembling

[41] A. Stock and K. Somieski, Ber., 1921, **54**, [B], 740; A., ii, 399.

silicic acid, and the value of x is certainly very high, since when the compound is produced in benzene solution, $x = 7$—8. When the benzene solution is evaporated, a viscous liquid is obtained which only slowly passes into the solid and more highly polymerised conditions.

The behaviour of the silylamines when treated with hydrogen chloride is very remarkable, because they are smoothly and quantitatively transformed into monochlorosilane and ammonium chloride.

When calcium silicide was carefully treated with cold dilute alcoholic hydrochloric acid in the dark, a white, solid substance was obtained together with a certain amount of hydrogen.[42] The white substance has the constitution $Si_2H\cdot OH$, and to it has been given the name of oxydisilin. It is a powerful reducing agent and is converted by means of bromine to silical bromide, Si_2OHBr. This substance is hydrolysed by water to silical hydroxide, a red compound which combines with strong acids to form salts that are yellow to red in colour. The silical compounds are all powerful reducing agents and they are decomposed by alkalis to form silica with evolution of hydrogen.

It has generally been believed that the coloured compounds obtained by the action of hydrogen peroxide on titanic salts are derivatives of the oxide, TiO_3. From estimations of the active oxygen it appears that these compounds are really complexes of hydrogen peroxide and pertitanic salts derived from the peroxide, Ti_2O_5.[43] The complex double potassium salt, $K_2SO_4,TiOSO_4$, was prepared, and when the salt was dissolved in ice-cold water and alcohol added, the clear liquid decanted from the precipitate was found to contain hydrogen peroxide. The addition of alcohol to a solution prepared by pouring equimolecular quantities of potassium sulphate and titanyl sulphate into an excess of hydrogen peroxide gave a precipitate of the hydrated peroxide, Ti_2O_5,xH_2O.

Some doubt has been thrown on the usually accepted explanation of the existence of the various forms of lead monoxide. This explanation is due to Ruer,[44] who stated that the forms are different allotropic modifications. It is now suggested that there is a much closer relationship between the forms, and, indeed, that the difference between them is due to variations in the size of the particles.[45] The red form of the oxide consists of particles, 3μ to 5μ, which, on being heated at $700°$ and then cooled, give yellow agglomerates, 10μ to 20μ. These easily break down under pressure to particles smaller

[42] H. Kautsky, Z. anorg. Chem., 1921, **117**, 209; A., ii, 505.
[43] M. Billy, Compt. rend., 1921, **172**, 1411; A., ii, 456.
[44] R. Ruer, Z. anorg. Chem., 1906, **50**, 265; A., 1906, ii, 755.
[45] S. Glasstone, T., 1921, **119**, 1689.

than those of the original red form, $0·7\mu$ to $1·5\mu$. The reddish-brown preparations consist of particles of the same order of magnitude as the finer particles of the yellow forms. All the forms give a brown powder on being ground in a mortar, the particles of which are uniformly $0·7\mu$ in diameter.

It is to be expected therefore that differences in solubility should be found depending on the size of the particles. The red form should have the lowest solubility and the reddish-brown forms should give higher values. This was proved to be the case by determination of the solubility of the various forms in a N-solution of sodium hydroxide free from carbonate.

The author makes no reference to the fact that the yellow form of lead monoxide is converted into the red form on exposure to light. This would lead to the conclusion that the difference is not only concerned with the size of the particles, but that there is a difference of energy content, at any rate between the yellow and red forms.

Group V.

Anhydrous ammonia and anhydrous chlorine react together to form nitrogen chloride and ammonium chloride, and the quantities that react do not change even when the relative proportions of the two reactants are varied between wide limits.[46] There is little or no reaction between chlorine and the solid ammonium chloride which is formed. A considerable proportion of the nitrogen chloride at first formed decomposes into nitrogen and chlorine, either directly or by interaction with ammonia.

Nitrogen chloride is quantitatively converted by dry hydrogen chloride into ammonium chloride, the action taking place in the presence or absence of an inactive solvent.[47] The reaction, therefore, is not one of hydrolysis and probably consists in the initial formation of trichloro-ammonium chloride, NCl_3HCl, which loses one positive atom and one negative atom of chlorine, the addition of hydrogen chloride and loss of chlorine taking place three times in succession. The formation of nitrogen chloride by the action of chlorine on an ammonium salt would seem to be the reverse of this reaction. For the preparation of nitrogen chloride ammonium sulphate is more suitable than ammonium chloride. Hypochlorous acid is preferable to free chlorine, because the use of the latter leads to the formation of some chloroamine and dichloroamine along with the nitrogen chloride.

Attempts were made to cause direct combination between

[46] W. A. Noyes and A. B. Haw, *J. Amer. Chem. Soc.*, 1920, **42**, 2167; *A.*, ii, 42.

[47] W. A. Noyes, *ibid.*, 2173; *A.*, ii, 42; *ibid.*, 1921, **43**, 1774.

nitrogen and chlorine by passing a mixture of the two gases through the flaming arc and also through an efficient ozoniser. No measurable combination took place, nor was there any reaction when active nitrogen was passed over chlorine at $-190°$.

An investigation has been made of the conditions under which the various compounds of ammonia and carbonic acid may be prepared from solutions of these two components.[48] Five compounds were obtained, and of these only one, $NH_4 \cdot HCO_3$, forms a true equilibrium in which the ratio between CO_2 and NH_3 is the same in the solution and in the solid phase. It was found that the double salt, $2NH_4 \cdot HCO_3,(NH_4)_2CO_3,H_2O$, crystallises from solutions containing NH_3 and CO_2 in the ratio $4:5$. Normal ammonium carbonate may be prepared by adding 395 grams of ammonium hydrogen carbonate to 150 grams of water and 333 grams of ammonia solution (25 per cent.) and passing in ammonia under an increased pressure of $0 \cdot 2$ atm. The mixture is warmed at $40°$ until solution is complete, when, on cooling to $10°$, the normal salt separates.

Solutions were prepared by dissolving each of the above salts and ammonium carbamate in aqueous ammonia of different concentrations, and these solutions were cooled to the temperature required. The range of temperature was from $0°$ to $60°$, and the following solid phases were identified between $0°$ and $33°$—$NH_4 \cdot HCO_3$; $2NH_4 \cdot HCO_3,(NH_4)_2CO_3,H_2O$; $(NH_4)_2CO_3$; $NH_4 \cdot HCO_3,NH_4 \cdot CO_2 \cdot NH_2$; $NH_4 \cdot CO_2 \cdot NH_2$. Of these, the normal carbonate and the two double salts have a limited temperature range of stability. Between $33°$ and $60°$, no further change was observed.

A convenient method for the storage of ammonia has been described [49] which is based on the fact that at $0°$ ammonium thiocyanate absorbs ammonia up to 45 per cent. of its weight. A widenecked bottle about 500 c.c. in capacity is fitted with a stopper carrying an inlet and outlet tube, each of which is provided with a stop-cock. The bottle is filled with the dry salt and is surrounded by ice, and the inlet tube connected with an ammonia generator, when the gas is very rapidly absorbed. After the salt has become saturated, the stop-cocks are closed and the bottle is placed in water and maintained at the ordinary temperature or a little above. The dry gas may then be drawn off as required. It is advisable to recharge the apparatus before the salt commences to crystallise from the liquid in order to guard against the blocking of the inlet tube.

[48] E. Terres and H. Weiser, *Z. Elektrochem.*, 1921, **27**, 177; *A.*, ii, 448.

[49] H. W. Foote and S. R. Brinkley, *J. Amer. Chem. Soc.*, 1921, **43**, 1178; *A.*, ii, 448.

By the addition of a solution of antimony trioxide in hydrochloric acid to a solution of sodium thiosulphate and the chloride of an alkali or alkaline-earth metal at about 3°, the stibio-thiosulphates are formed.[50] The salts may be crystallised at low temperatures or precipitated by the addition of alcohol. The reaction proceeds according to the equation $SbOCl + 2HCl + 3K_2S_2O_3 = 3KCl + H_2O + K_3Sb(S_2O_3)_3$, and the constitution of the salt is represented by $Sb(S \cdot SO_2 \cdot OK)_3$. The sodium salt is extremely soluble and has not been prepared in the solid state. The potassium salt forms silk-like, needle-shaped crystals, very similar in appearance to asbestos. The barium salt is white and not very stable. It quickly becomes yellow and finally very deep yellow in colour, owing to decomposition. The potassium salt, on heating, decomposes according to the equation $2K_3Sb(S_2O_3)_3 = Sb_2S_3 + 3K_2SO_4 + 3SO_2 + 3S$. The aqueous solution, when boiled, decomposes with deposition of the orange-red compound, Sb_2OS_2.

The corresponding potassium arseno-thiosulphate,[51] $K_3As(S_2O_3)_3$, has been prepared in an exactly analogous manner. It is a white substance which is not very stable when moist. Its aqueous solution, on boiling, decomposes to give potassium trithionate according to the equation

$$(KO \cdot SO_2 \cdot S)_3As + As(S \cdot SO_2 \cdot OK)_3 = As_2S_3 + 3KO \cdot SO_2 \cdot S \cdot SO_2 \cdot OK,$$

and from this it would seem that trithionic acid has the persulphide formula.

Group VI.

It is known that by the action of ozone on sodium hydroxide and potassium hydroxide orange-coloured products are obtained which are believed to be ozonides or higher oxides.[52]   Attempts have been made to prepare these substances by the action of ozone on solutions of the alkali and alkaline-earth metals in liquid ammonia.[53] Although the compounds were precipitated, difficulties were caused by the action of ozone on ammonia. The ozonides, therefore, could not be obtained in a pure state. They are readily decomposed by water and dilute acids with evolution of oxygen and formation of hydrogen peroxide. The ozonides of rubidium and cæsium are more stable than the sodium, potassium, calcium, and barium compounds.

It was found that ozone is quantitatively reduced by liquid ammonia, the products being about 98 per cent. of ammonium nitrate and 2 per cent. of nitrite. The first action of the ozone is to

[50] J. v. Szilágyi, Z. anorg. Chem., 1920, 113, 69; A., ii, 207.

[51] Idem, ibid., 75; A., ii, 199.

[52] W. Traube, Ber., 1912, 45, 2201; A., 1912, ii, 844.

[53] W. Strecker and H. Thienemann, ibid., 1920, 53, [B], 2096; A., ii, 44.

produce an orange colour, which may be due to an unstable ozonide. Ozone also reacts with methylamine, dimethylamine, and trimethylamine. In the last case, the reaction is explosive, even at $-60°$. A 5—10 per cent. solution of trimethylamine in chloroform gives on treatment with ozone trimethylamine oxide, $O\dot{.}N(CH_3)_3$, which is precipitated as the hydrochloride, the hydrogen chloride being formed by the action of ozone on chloroform.

Very stable colloidal solutions of selenium [54] may be prepared by the regulated action of concentrated hydrazine hydrate solution on selenium dioxide or grey, crystalline selenium, and subsequent dilution of the solutions with water and purification by dialysis. These solutions vary in colour from intense yellow to blood-red, and when dilute are stable at the boiling point.

When selenium sols produced by the action of sulphur dioxide on solutions of selenious acid at 60° are frozen, the destruction caused by the freezing is greater the more completely the solutions have been purified by dialysis.[55] Even although the solutions are completely frozen, the greater part of the colloid goes back into solution after melting. If the freezing is repeated many times, or if the solution is kept in the frozen condition too long, the colour by transmitted light becomes less intense and the stability of the sol becomes much less, particularly towards an increase in temperature. The nature of the reducing agent employed in the preparation of the sols and the temperature of preparation have a great influence on the stability toward freezing. Sols prepared by reduction with hydrazine at 60° and dialysed are much more sensitive to freezing than those prepared by reduction with sulphur dioxide at the ordinary temperature. The hydrazine sols coagulated irreversibly on cooling even before solidification occurred. In the case of the sulphur dioxide sols, the concentration of the undialysed sol has a marked influence on the stability towards a reduction of temperature. The more concentrated sols are more readily destroyed by freezing than the more dilute solutions.

Three methods have been given for the preparation of selenium oxychloride.[56] Selenium in solution in carbon tetrachloride is treated with chlorine. Selenium monochloride is first formed and remains dissolved in the carbon tetrachloride. If any metallic impurities in the selenium are present, these are precipitated as chlorides and may be separated by filtration at this stage. The solution is then saturated with chlorine and selenium tetrachloride is precipitated. The calculated quantity of selenium dioxide is

[54] A. Gutbier and R. Emslander, *Ber.*, 1921, **54**, [*B*], 1974; *A.*, ii, 636.

[55] A. Gutbier and F. Flury, *Kolloid Z.*, 1921, **29**, 161; *A.*, ii, 693.

[56] V. Lenher, *J. Amer. Chem. Soc.*, 1920, **42**, 2498; *A.*, ii, 109.

added, when selenium oxychloride is formed and the whole passes into solution. The selenium oxychloride may readily be separated from the carbon tetrachloride by fractionation. Since selenium oxychloride readily dissolves selenium, the preparation may very conveniently be carried out by mixing equivalent quantities of selenium and selenium dioxide, adding selenium oxychloride, and treating the mixture with chlorine.

The second method consists in the partial hydrolysis of selenium tetrachloride, which may be carried out with the solid tetrachloride or with the tetrachloride suspended in carbon tetrachloride or selenium oxychloride.

The third method is the dehydration of the compound $SeO_2,2HCl$, which is an amber-coloured liquid and can be prepared by treating selenium dioxide with dry hydrogen chloride at moderately low temperatures. The liquid is mixed with an excess of phosphoric oxide or calcium chloride, and the oxychloride obtained by distillation. Alternatively, selenium dioxide may be mixed with the dehydrating agent and treated with hydrogen chloride in the cold. On heating the mixture, the selenium oxychloride passes off.

Selenium oxychloride is a nearly colourless liquid with b. p. 176·4° at 726 mm. and m. p. 8·5°.[57] Amongst many interesting properties of this substance the following may be mentioned. Sulphur, selenium, and tellurium dissolve readily in cold selenium oxychloride, but when the solutions are heated complicated reactions take place. Red phosphorus reacts with selenium oxychloride in the cold with evolution of light and heat, whilst with yellow phosphorus the reaction is explosive. Bromine and iodine give solutions which are very reactive and are coloured reddish-brown and violet respectively. Boron, silicon, and carbon are not attacked in the cold.

Most of the metals are attacked by selenium oxychloride with formation of the chloride of the metal and selenium monochloride, Se_2Cl_2. There is a remarkable difference in the behaviour of sodium and potassium with the oxychloride. No action takes place with sodium, indeed the oxychloride may be distilled off this metal. Potassium, on the other hand, when brought into contact with selenium oxychloride in the cold, explodes with great violence. Aluminium, zinc, bismuth, and tin are readily attacked, whilst only slow reaction takes place with calcium, copper, magnesium, chromium, lead, nickel, arsenic, cadmium, cobalt, gold, and platinum. Powdered antimony takes fire when introduced into the liquid.

Selenium oxychloride dissolves selenium dioxide to a limited

[57] V. Lenher, *J. Amer. Chem. Soc.*, 1921, **43**, 29; *A.*, ii, 256.

extent. It also dissolves arsenious oxide, vanadium pentoxide, and molybdenum trioxide, all of which are chemically acted on. The solution of molybdenum trioxide shows a striking photochemical reaction, for on exposure to bright light it becomes blue in a few minutes, the solution regaining its original pale yellow colour within a few hours when kept in a subdued light. Sulphur trioxide dissolves in selenium oxychloride to form a viscous, heavy solution which has powerful solvent properties. It dissolves the oxides of aluminium, chromium, titanium, columbium, molybdenum, vanadium, uranium, and the rare earths; it dissolves the oxide of titanium very slowly and has no action on the oxides of zirconium and tungsten.

The same care is required in handling selenium oxychloride as with any other highly corrosive liquid. Its vapour has no other physiological action than that of the hydrogen chloride produced by its hydrolysis.

Group VII.

Some interesting work has been carried out on the equilibria of hydrofluosilicic acid.[58] When a solution of hydrofluoric acid was titrated against sodium hydroxide with phenolphthalein as indicator, an apparently considerable excess of alkali could be run in and yet the colour disappeared again after a few seconds. It was found that this was due to the presence of hydrofluosilicic acid, even although the hydrofluoric acid was of A.R. standard.

A method of investigation of the proportions in which the two acids are present in the mixture was described by Katz,[59] and consists in the precipitation of potassium silicofluoride by the addition of potassium chloride solution followed by alcohol. The solution, after filtration, is titrated, and, further, an equal volume of the original solution is titrated, phenolphthalein being used as indicator in each case. The method is rendered inaccurate by the adsorption of some hydrogen fluoride by the colloidal potassium silicofluoride. For the complete neutralisation of hydrofluosilicic acid according to the equation $H_2SiF_6 + 6NaOH = 6NaF + H_2SiO_3 + 3H_2O$, an appreciable time is required,[60] and it has now been found that this is due to the relatively slow dissociation of sodium silicofluoride according to the equation $Na_2SiF_6 = 2NaF + SiF_4$, it being proved that the reaction is unimolecular. This has enabled a determination to be made of the composition of mixtures

[58] L. J. Hudlestone and H. Bassett, *T.*, 1921, **119**, 403.
[59] J. Katz, *Chem. Zeit.*, 1904, **28**, 356, 387; *A.*, 1904, ii, 442.
[60] C. R. Wagner and W. H. Ross, *J. Ind. Eng. Chem.*, 1917, **9**, 1116.

of the two acids. When silicon tetrafluoride is passed into water, the reaction may be expressed by the equations :—
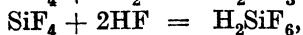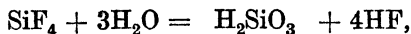
$$SiF_4 + 3H_2O = H_2SiO_3 + 4HF,$$
$$SiF_4 + 2HF = H_2SiF_6,$$
and
$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3,$$
by addition.

The reactions must be reversible, since hydrofluosilicic acid is formed equally by the action of silicon tetrafluoride on water and of hydrofluoric acid on silica, and also hydrofluosilicic acid with sufficient alkali yields, ultimately, sodium fluoride and silicic acid. Therefore all four substances must be present in finite, even although possibly very small, concentration in these solutions. Further, these solutions, filtered from the precipitated silicic acid, on titration by Katz's method, react like pure hydrofluosilicic acid, so that the free hydrofluoric acid cannot be·in excess of that required to combine with the free silicon tetrachloride and silicic acid to form hydrofluosilicic acid.

A determination of the amounts present in a solution which in total acidity was $0·05N$ showed the following—SiF_4 0·0005 mol. per litre, H_2SiF_6 0·0045 mol. per litre, and HF 0·021 mol. per litre. It was also proved that the silicic acid must be present in true solution, since its active mass varies with dilution in the ordinary way.

When a mixture of potassium perchlorate (3 parts) and chlorosulphonic acid (5 parts) is gradually heated to 70—75° in a vacuum, a mixture of chlorine heptoxide and pyrosulphuryl chloride passes over.[61] Pale yellow chlorine heptoxide (98—99 per cent.) is prepared by the distillation of the product in a vacuum, but traces of sulphur compounds are obstinately retained even after repeated distillation. The process is almost free from danger.

Chlorine heptoxide in a higher state of purity can be obtained by the very cautious addition of phosphoric oxide to strongly-cooled perchloric acid (70 per cent.) in such a manner that the heptoxide can ultimately be distilled, but local overheating cannot be avoided and the yields are poor. Pure solutions of chlorine heptoxide in carbon tetrachloride may be prepared by this method. Considerable amounts of phosphoric oxide are suspended in carbon tetrachloride, the mixture is cooled to 0° and violently stirred, while perchloric acid is added drop by drop. The mixture is warmed and filtered and yields a solution containing about 2·5 per cent. of chlorine heptoxide. If this solution is distilled as far as possible at 0° in a water-pump vacuum, a residue remains which contains about 1/3 of the original carbon tetrachloride and 80 per cent. of the heptoxide.

[61] F. Meyer and H. G. Kessler, *Ber.*, 1921, **54**, [*B*], 566; *A.*, ii, 326.

A colloidal solution of manganese dioxide may conveniently be prepared by the reduction of dilute solutions of potassium permanganate by means of ammonia.[62] A $N/20$-solution of potassium permanganate is heated to the boiling point and, while stirring, concentrated ammonia solution is added at the rate of one drop every three or four minutes. At no time should anything but the faintest smell of ammonia be perceptible. The solution gradually turns wine-red and finally becomes coffee-brown. To test if all the permanganate has been reduced, a little of the colloidal solution may be coagulated by the addition of sodium chloride to show the presence of any violet colour which might have been masked by the colloid. The product only contains potassium hydroxide as an impurity, and as this substance has no action on the colloid, it may be left in the solution. This eliminates the necessity of removing the electrolyte by dialysis, especially since the colloid is coagulated by filter paper or parchment. The colloid at all concentrations catalyses the decomposition of hydrogen peroxide. The concentrated solutions are coagulated during the reaction, whilst dilute solutions are unaffected. The colloid is perfectly stable in the presence of alcohol of all concentrations.

Group VIII.

The formation of sodium ferrite and ferrate by electrolysis of sodium hydroxide solution with iron anodes has been investigated,[63] and it is found that these salts only are formed, since the iron passes into solution only in the bivalent or sexavalent condition. Sodium ferrite may also be obtained by cathodic reduction of a solution of sodium ferrate. Measurements of the equilibrium potential of iron against a sodium ferrite solution and of platinum against mixtures of ferrite and ferrate show that the ferrite solution is more complex than is represented by the simple formula Na_2FeO_2.

Commercial platinum may be freed from the impurities it usually contains by repeated precipitation as ammonium platinichloride.[64] It was found that a sample of platinum containing palladium, rhodium, and iridium, as well as considerable amounts of tin, iron, and other metals, can be obtained in the pure state by four such precipitations. Each precipitate of ammonium platinichloride is drained on a Buchner funnel, stirred with a considerable volume of 15—20 per cent. ammonium chloride solution, and again drained, this process being repeated two or three times. The washed pre-

[62] E. J. Guy, *J. Physical Chem.*, 1921, **25**, 415; *A.*, ii, 642.

[63] G. Grube and H. Gmelin, *Z. Elektrochem.*, 1920, **26**, 459; *A.*, ii, 49.

[64] E. Wichers, *J. Amer. Chem. Soc.*, 1921, **43**, 1268; *A.*, ii, 648.

cipitate is dried, ignited to platinum sponge in an electrically heated muffle, and dissolved in aqua regia. The solution is evaporated several times with hydrochloric acid to remove nitric acid and precipitated with ammonium chloride. The amount of platinum left in the mother-liquor from the precipitate is usually not more than 1 per cent. of that in the precipitate. The final precipitate is ignited to sponge in a porcelain dish over a gas flame in a current of hydrogen.

In the Reports for the last two years reference was made to work on the occlusive power of platinum and palladium for hydrogen, and brief mention may be made of some further investigations. In the first place, it has been confirmed that the amount of hydrogen occluded by palladium is determined by the relative amounts present of the two forms of the metal, the amorphous and the crystalline.[65] In all probability this explains the divergent results obtained by Hemptinne [66] and by Paal and Amberger,[67] since the occlusive power of the crystalline variety is very much reduced at low temperatures.

In last year's Report the reporter criticised Dr. Maxted's interpretation of the results he obtained on the poisoning of palladium by hydrogen sulphide, and suggested that the adsorption of hydrogen consists of two separate processes, first, the occlusion of hydrogen as atoms, followed by a secondary effect of condensation as molecules. Dr. Maxted has now brought forward evidence which strongly supports this view, and, moreover, brings the results more into agreement with the modern views of catalytic activation by metals.[68] This is well shown by the results obtained on the poisoning of palladium by lead, in which for a known lead content both the occlusive power for hydrogen and the catalytic activity of the product were measured. The catalytic activity is a linear function of the lead content up to a stage in which the greater part of the activity has been suppressed. A point of inflection occurs at this stage, below which the decrease of activity caused by further addition of lead falls off far less steeply. The occlusive power for hydrogen is also a linear function of the lead content, but the slope of the two lines is very different. Thus, a ratio of 0·17 gram-atom of lead to 1 gram-atom of palladium is required to reduce the occlusive power to one-half, whilst in order to reduce the catalytic activity to one-half, only about 0·02 gram-atom of lead to each

[65] J. B. Firth, *T.*, 1921, **119**, 1120.

[66] A. de Hemptinne, *Bull. Acad. roy. Belg.*, 1898, [iii], **36**, 155; *A.*, 1899, ii, 228.

[67] C. Paal and C. Amberger, *Ber.*, 1905, **28**, 1394; *A.*, 1905, ii, 397.

[68] E. B. Maxted, *T.*, 1920, **117**, 1501; 1921, **119**, 1280.

gram-atom of palladium is necessary. It is probable therefore that, whilst the occlusion is not confined to the surface only of the palladium, catalysis is mainly a surface phenomenon. This view is strengthened by the fact that the slope of the poisoning line for catalytic activity varies with the fineness of division of the catalyst.

It is evident from these observations that, as suggested, there are two processes, namely, the adsorption and activation of the hydrogen on the surface of the catalyst, and the condensation of more hydrogen as molecules within the capillaries. Apart from the bearing of this on Dr. Maxted's previous work, it has considerable importance from the energy side, since energy must be given to the hydrogen molecules in order to activate them. This energy must be supplied by the palladium, and it is not possible to believe that this action can extend beyond a molecular layer of hydrogen distributed over the surface of the metal. In this connexion recent experimental work tends more and more to show that in all similar cases of heterogeneous catalysis the thickness of the activated layer is of molecular dimensions.

By the reduction of sodium platinichloride with an excess of sodium hyposulphite a dark reddish-brown solution is obtained which, on slow evaporation, deposits a precipitate which is a complex mixture of sodium platinosulphite compounds with $Na_2Pt_4S_6$.[69] After filtration, the solution first deposits crystals of sodium platinisulphite, $Na_4[Pt(SO_3)_3(OH)_2],H_2O$, and then, on further evaporation, bright yellow crystals of sodium platinothiosulphate,
$$Na_5[Pt(S_2O_3)_4],10H_2O.$$
By reduction of iridium tetrachloride in neutral solution sodium iridosulphite, $Na_6[Ir(SO_3)_4],10H_2O$, was obtained in bright yellow crystals. The following salts were also prepared,
$$Na_6[Rh_4(SO_3)_7],12H_2O;\ Na_6[Os_4(SO_3)_7],24H_2O, and Na_3H_3[Ru(SO_3)_4].$$
<div align="right">E. C. C. BALY.</div>
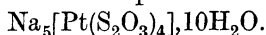
[69] G. Sailer, *Z. anorg. Chem.*, 1921, **116**, 209; *A.*, ii, 513.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

THE usual arrangement of this division of the Annual Reports has been followed, except that the section dealing with optical activity has been omitted this year as only a few papers on the subject have appeared.

Hydrocarbons.

The problem of converting natural paraffin into a mixture of fatty acids is still receiving attention, although apparently very little progress has been made. Schaarschmidt and Thiele [1] chlorinate paraffin at 160° and then remove hydrogen chloride either by treatment with alkali or by simply heating at about 300°; the resulting mixture of olefines is then oxidised, preferably by ozone, and under the best conditions a yield of about 60 per cent. of the higher fatty acids is obtained. No better results were obtained by Gränacher,[2] who oxidised heated paraffin wax by a current of air containing 2 per cent. of nitrogen peroxide. At 150°, the process requires about four days. When n-undecane is treated in the same manner, nonoic is the highest acid formed, and this only in small quantity. The method is therefore unsuitable for the degradation of hydrocarbons, but shows that the higher paraffins in nature must consist only to a small extent of normal hydrocarbons.

The combination of acetylene with water in the presence of various catalysts to form acetaldehyde has again been investigated, mainly because of the difficulty of regenerating the catalysts; this can be done, when oxides such as molybdic acid are used, by a current of air at a high temperature [3] or by the periodic addition of ferric oxide to a heated solution of mercuric sulphate.[4] In this connexion, the discovery by W. J. Jenkins [5] of a new compound of acetylene and mercuric chloride, $HgCl_2,2C_2H_2$, which contains double the amount of acetylene to that in the well·known compound,

[1] Ber., 1920, 53, [B], 2128; A., i, 1.
[2] Helv. Chim. Acta, 1920, 3, 721; A., i, 2.
[3] D. R.-P. 334357; A., i, 542.
[4] Brit. Pat. 140784; A., i, 706.   [5] T., 1921, 119, 747.

may be of some practical interest. Kindler [6] has observed that gold is quantitatively precipitated from dilute solutions of the auric haloids by acetylene, which is thereby converted into glyoxal.

Alcohols and Derivatives.

Very little research has been published on alcohols during the year, but a few new methods of preparation are of interest.

Methyl alcohol [7] is readily purified from acetone by taking advantage of the fact that methyl alcohol and chloroform form a binary mixture boiling at 53° at atmospheric pressure. In practice, 1 part of the crude alcohol is mixed with 7·5 parts of chloroform, the mixture distilled, and then from the fraction boiling at about 53° the methyl alcohol is extracted by water, the aqueous alcohol being rectified in the usual manner.

Acetaldehyde [8] can be reduced in an economical manner if led into the cathode chamber of an electrolytic cell charged with a suitable acid medium in such a manner that the concentration of the acetaldehyde in the solution is maintained low. When this does not exceed about 5 per cent. the yield of alcohol is good and the current efficiency high.

The preparation of primary alcohols by the action of Grignard's reagents on trioxymethylene is rendered very tedious by its sparing solubility in ether and its very gradual depolymerisation. The usual small yields are much improved [9] and the time required is much shortened if the vapours from well-dried boiling trioxymethylene are led into a well-stirred Grignard reagent. The yield of the alcohols, $R \cdot CH_2 \cdot OH$, is reduced when R is small (particularly when $R = C_2H_5$), owing to the formation of considerable quantities of the methylene ethers, $CH_2(OR)_2$.

Secondary butyl alcohol is very easily prepared from the butylene formed by the catalytic dehydration of n-butanol. The liquefied β-butylene [10] is mixed with 75 per cent. sulphuric, with phosphoric or with benzenesulphonic acid, either at the ordinary temperature under increased pressure or at $-10°$ under atmospheric pressure. When absorption of the hydrocarbon is complete, the liquid is diluted with water and the secondary alcohol distilled over with a current of steam.

Many of the preparations carried out by modern methods of

[6] *Ber.*, 1921, **54**, [*B*], 647; *A.*, i, 396.

[7] A. Lanzenberg and J. Duclaux, *Bull. Soc. chim.*, 1921, [iv], **29**, 135; *A.*, i, 298.

[8] Chem. Fabrik Greisheim Elektron, D. R.-P. 328342; *A.*, i, 155.

[9] K. Ziegler, *Ber.*, 1921, **54**, [*B*], 737; *A.*, i, 394.

[10] C. Weizmann and D. A. Legg, Brit. Pat. 161591; *A.*, i, 493.

catalysis at high temperatures are unsatisfactory owing to contamination with small amounts of impurities formed by isomeric change under the influence of the catalyst. This phenomenon is well illustrated by a quantitative study of the products of the dehydrogenation of the mixture of amyl alcohols produced by fermentation. Using aluminium silicate heated at 350° as the catalyst, Senderens [11] has shown that the relative proportion of the three hydrocarbons, β-methyl-Δ^β-butene, β-methyl-Δ^α-butene, and γ-methyl-Δ^α-butene, the last two of which may be assumed to be formed direct from the β-methylbutan-α-ol, $CH_3 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot OH$, and from the *iso*butylcarbinol respectively, varies considerably with the age of the catalyst. In the fermentation alcohol there is generally about 87 per cent. of *iso*butylcarbinol and 13 per cent. of the optically active constituent, but the proportion of γ-methyl-Δ^α-butene is always very much less than that of the β-methyl isomeride. When the catalyst is new and active, nearly four-fifths of the product consists of β-methyl-Δ^β-butene obviously formed by isomeric change from β-methyl-Δ^α-butene under the influence of the catalyst, since, when this ages, the proportion of these two hydrocarbons in the product becomes nearly equal, whilst that of the γ-methyl-Δ^α-butene, which is only one-thirtieth with the fresh catalyst, amounts to one-fifth of the product.

The proportion of the various isomerides may, moreover, depend on the pressure, for Moureu and Mignonac [12] have shown that this affects the dehydrogenation of alcohols when this is carried out by contact with oxygen and finely divided silver at 230—300°.

The reaction between alcohols and hydrogen sulphide to form mercaptans [13] is brought about by specially prepared thorium oxide at 380°. The catalyst needs to be formed from the nitrate by decomposition of this in a current of air at 270°, and thus differs from the ordinary thoria commonly used as a catalyst in other reactions. The yields amount to 40 to 50 per cent. when the vapour of the alcohol and the hydrogen sulphide are passed over the catalyst at the rate of 1 gram-molecule per hour. The mercaptans give mixtures of constant boiling point with the corresponding alcohols and are best purified by means of their lead salts.

Acids and their Derivatives.

It is well known that the acetylating action of acetic anhydride is often increased by the addition to it of traces of concentrated

[11] *Compt. rend.*, 1920, **171**, 916; *A.*, i, 4.

[12] *Ibid.*, 652; *A.*, 1920, i, 805.

[13] R. L. Kramer and E. E. Reid, *J. Amer. Chem. Soc.*, 1921, **43**, 880; *A.*, i, 389.

sulphuric acid. This is probably due to the formation of small amounts of acetylsulphuric acid, $CH_3 \cdot CO \cdot O \cdot SO_2 \cdot OH$, the preparation and properties of which have been described by van Peski.[14] It is formed when sulphur trioxide acts on acetic acid at $0°$, and reacts with sodium acetate to form sodium acetylsulphate. This salt, when heated, decomposes, giving sodium pyrosulphate and acetic anhydride, but when heated with acetic acid gives acetic anhydride and sodium hydrogen sulphate, a reaction which is reversible. When heated at $70°$, acetylsulphuric acid is converted into sulpho-acetic acid, which is readily acetylated by acetylsulphuric acid, forming acetylsulphoacetic acid; the latter readily condenses to

form disulpho-dehydroacetic acid, $\begin{matrix} CH_3 \cdot CO \\ SO_3H \end{matrix} > C < \begin{matrix} CO \cdot O \cdot CMe \\ CO — C \cdot SO_3H \end{matrix}$.

Acetylsulphuric acid is a very vigorous acetylating agent, acetylating, for example, tribromophenol with ease; in some cases, however, it acts as a sulphonating agent, converting benzene, for example, into benzenesulphonic acid.

Acetylene will combine with acetic acid to form ethylidene diacetate quantitatively under certain conditions in the presence of a variety of catalysts. The best of these appear to be methylene sulphate at about $50°$, methyl sulphate [15] at about $75°$, or mercury naphthalene-β-sulphonate [16] at a temperature of about $50°$.

Zirconium oxide [17] must be added to the list of substances which are capable of bringing about the condensation of the vapours of acids and alcohols to form esters. This catalyst works best at a temperature of $270—290°$, whilst the yield of ester depends on the weight of oxide used, the velocity of the flow of the vapours, and the proportion of acid and alcohol used.

There have been many observations of interaction between esters and alcohols in the presence of catalysts, leading to the formation of new esters. Attention was directed by Fischer [18] to the fact that glycerol α-monobenzoate is moderately rapidly converted in ethereal solution in the presence of potassium carbonate into a mixture of glycerol and a dibenzoate. The process is more conveniently followed with the benzoyl derivatives of ethylene glycol in chloroform solution, whereby it is shown that the change is balanced and attains an equilibrium in the presence of the glycol and the mono- and di-benzoates. Similarly, glycerol monoacetate is largely transformed

[14] *Rec. trav. chim.*, 1921, **40**, 103; *A.*, i, 302.

[15] D. R.-P. 322746; *A.*, 1920, i, 810.

[16] *Ibid.*, 334554; *A.*, i, 535.

[17] A. Mailhe and F. de Godon, *Bull. Soc. chim.*, 1921, [iv], **29**, 101; *A.*, i, 219.

[18] E. Fischer, E. Pfähler, and F. Brauns, *Ber.*, 1920, **53**, [B], 1634; *A.*, 1920, i, 840.

into diacetin and glycerol. The action of the potassium carbonate appears to be definitely catalytic, since very small amounts of it suffice to accelerate the change. The phenomena recorded in this paper are very similar to those first observed by Purdie,[19] who found that an exchange of alkyl radicles readily took place between simple esters and alcohols in the presence of a small amount of sodium alkyloxide. Grün[20] has now shown that this interchange of alkyl groups between fats and alcohols can take place under certain conditions even in the absence of catalysts.

Such phenomena explain to some extent the gradual change in melting point observed by Grün to take place when diacyl derivatives of glycerol are preserved and also of the so-called " ageing " of the natural fats. This, however, is not a complete explanation of all the facts, as some of the triglycerides are known in more than one form, as, for example, tristearin, which exists in two forms, m. p. 55° and 71° respectively. Grün prefers to regard these as examples of co-ordination isomerism, in which most of the esters (fats) may be regarded as an equilibrium mixture of the forms $R\cdot C\!\!<^{O}_{OR'}$ and $R\cdot C\!\!<^{O}_{O}\!\!\big\}R'$. According to the author's views, then, a mono-glyceride can exist in two forms, $(OH)_2C_3H_5\cdot O\cdot C\!\!<^{O}_{R}$ and $(OH)_2C_3H_5\!\cdots\!O_2CR$, a diglyceride in three forms,

$$HO\cdot C_3H_5\Big(O\cdot C\!\!<^{O}_{R}\Big)_2, \quad HO\cdot C_3H_5\!\!<^{\diagup^{O}\!\!>CR}_{\diagdown O-C\!\!<^{O}_{R}}, \quad \text{and} \quad HO\cdot C_3H_5\!\!<^{\diagup^{O}\!\!>CR}_{\diagdown_{O}\!\!>CR}$$

whilst a triglyceride formed from a single acid can exist in four forms, namely, the ordinary ester and pure co-ordination varieties and two mixed types. Thus the co-ordination form of a triglyceride formed from a single acid only can pass into the true ester form, but from the co-ordination form of a mixed triglyceride, a mono- or a di-glyceride, all the structural isomerides can, in addition, be produced. This hypothesis, although somewhat intangible, does serve to correlate the numerous and otherwise confusing facts which are recorded in the author's papers, and is very similar to those put forward by other investigators to explain the abnormal physical properties of some esters.

The phenomena described in the preceding paragraphs render the synthesis of pure glycerides a matter of some considerable difficulty. For this reason, a method for the synthesis of optically active αβ-

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[19] T. Purdie, *T.*, 1887, **53**, 391.

[20] A. Grün, F. Wittka, and J. Scholze, *Ber.*, 1921, **54**, [B], 273, 290; *A.*, i, 220, 222.

diglycerides and unsymmetrical triglycerides in which the position of the respective acyl groups is tolerably certain is very welcome. Such a synthesis which, although somewhat complex, seems to avoid the possibility of the interchange of acyl groups, is described by M. Bergman and his co-workers.[21] The starting point is γ-amino-$\alpha\beta$-propylene glycol, which is readily obtained by the action of ammonia on glycide. The aminoglycol is first of all condensed with benzaldehyde, thus forming 2-phenyl-5-hydroxymethyloxazolidine,

$$OH\cdot CH_2\cdot CH \underset{O—CHPh}{\overset{CH_2\cdot NH}{<}|}.$$ This contains one alcoholic hydroxyl

group, which can be acylated. The ring in the resulting acylated compound is readily opened up with the elimination of benzaldehyde, giving compounds of the formula $OA\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NHA$. These can be treated with another acylating agent, giving compounds of the type $OA\cdot CH_2\cdot CH(OB)\cdot CH_2\cdot NHA$. Mild treatment with phosphorus pentachloride and water converts these into compounds of the type $OA\cdot CH_2\cdot CH(OB)\cdot CH_2\cdot NH_2$, which can be resolved into their optically active components. By treatment with nitrous acid, there are obtained $\alpha\beta$-diglycerides, $OA\cdot CH_2\cdot CH(OB)\cdot CH_2\cdot OH$, which can be converted into unsymmetrical triglycerides. The presence of two asymmetric carbon atoms in the oxazolidine does not interfere with these syntheses, as one disappears on removal of the benzaldehyde when the ring is ruptured.

So far, the syntheses have been carried out only with benzoyl and nitro- and chloro-substituted benzoyl groups as acylating agents. The resolution of γ-aminopropylene $\alpha\beta$-dibenzoate was effected by crystallisation of its quinate, and after treatment with nitrous acid gave the oily l-glycerol $\alpha\beta$-dibenzoate. This was further treated with p-nitrobenzoyl chloride, giving l-glyceryl $\alpha\beta$-dibenzoate γ-p-nitrobenzoate with m. p. 114° and with $[\alpha]_D - 1\cdot9°$ in s-tetra-chloroethane. This compound is claimed by the authors to be the first example of the synthesis of a homogeneous, optically active triglyceride. It may be pointed out, however, that the homogeneous character of their preparation is not definitely proved, whilst the low rotation may be caused by racemisation during its production.

M. Tsujimoto [22] has observed that the lithium salts of the more highly unsaturated acids derived from fish oils are readily soluble in acetone containing 5 per cent. of water, and since those of the saturated or slightly unsaturated acids are insoluble in this solvent a separation can be effected and gives amounts of highly unsaturated acids which are considerably higher than those calculated from the yields of the polybromides.

[21] *Ber.*, 1921, **54**, [*B*], 936; *A.*, i, 444.
[22] *J. Chem. Ind. Japan*, 1920, **23**, 1007; *A.*, i, 78.

For the synthesis of the basic derivatives of cocaine, succinyl-diacetic acid is a convenient starting point. A satisfactory preparation of this acid has been described by Willstätter and Pfannenstiel,[23] who have obtained the dipotassium derivative of the enolic form of ethyl hydrogen acetonedicarboxylate, $CO_2Et \cdot CH_2 \cdot C(OK) \colon CH \cdot CO_2K$. A solution of this compound, after neutralisation by oxalic acid of the enolic potassium, is readily converted by electrolysis into the diethyl ester of the required acid, $C_2H_4(CO \cdot CH_2 \cdot CO_2Et)_2$, which shows the properties of an enol and exhibits the reactions of a β-ketonic ester. The acid and its esters readily condense with amines to give pyrrole derivatives of the type $NMe {<} {C(CH_2 \cdot CO_2Et) \colon CH \atop C(CH_2 \cdot CO_2Et) \colon CH}$.

In last year's Report, the successful separation was described of the keto-form of ethyl acetoacetate by K. Meyer and co-workers, who fractionated the equilibrium mixture in specially cleaned distillation flasks of quartz under a pressure of 2 mm. The isolation of the pure enol form is now described.[24] For this purpose, the equilibrium ester is distilled from a Jena glass flask in the presence of a trace of phthalic acid. The distillate, which is collected in a quartz receiver, contains nearly 90 per cent. of the enol and is immediately refractionated from a silica apparatus, the first fraction being composed of the pure enol. Similar results have been obtained by distillation of acetylacetone, which, however, appears to be far more sensitive than ethyl acetoacetate to the influence of catalysts.

Ingold [25] has investigated the mechanism underlying the reaction of ethyl cyanoacetate with tautomeric compounds and shown that in the great majority of cases the first stage is the addition of the cyano-ester to the double bond. This in all probability is the reason why the polyacetic acids of methane such as the triacetic acid, $CH(CH_2 \cdot CO_2H)_3$, carboxytriacetic acid, $CO_2H \cdot C(CH_2 \cdot CO_2H)_3$, and the tetra-acetic acid, $C(CH_2 \cdot CO_2H)_4$, are all difficult to prepare, since the corresponding unsaturated acids, $CO_2H \cdot CH \colon CH \cdot CH_2 \cdot CO_2H$, $CO_2H \cdot CH \colon C(CO_2H) \cdot CH_2 \cdot CO_2H$, and $CO_2H \cdot CH \colon C(CH_2 \cdot CO_2H)_2$, are all substances of the glutaconic acid type with a mobile hydrogen atom—a series of compounds which have been shown by J. F. Thorpe and his co-workers to be exceedingly unreactive and not unsaturated in the ordinary sense of the term. Methanetriacetic acid,[26] however, can be prepared readily by the condensation of ethyl sodiocyanoacetate with diethyl β-hydroxyglutarate and subsequent hydrolysis of the product. Further investigation [27] of

[23] *Annalen*, 1921, **422**, 1; *A.*, i, 91.

[24] K. H. Meyer and H. Hopff, *Ber.*, 1921, **54**, [*B*], 579; *A.*, i, 391.

[25] C. K. Ingold, *T.*, 1921, **119**, 329.

[26] *Idem, ibid.*, 346.

[27] C. K. Ingold and E. A. Perren, *ibid.*, 1582.

the condensation of highly substituted glutaconic esters and ethyl cyanoacetate shows that in derivatives of methanetriacetic acid substituents in more than one of the acetic acid chains produce a condition of instability.

Constitution of Grignard's Magnesium Compounds.

The various formulæ, $\mathrm{Et\!\!>\!\!O\!\!<\!\!^{MgAlk}_{Hal}}$, $\mathrm{Et\!\!>\!\!O\!\!<\!\!^{Alk}_{MgHal}}$, and $\mathrm{Et\!\!>\!\!O\!\!<\!\!^{MgAlk}_{Hal\cdot OEt_2}}$, which have from time to time been assigned to Grignard's reagents must be regarded as unsatisfactory, since they fail to account for the full reactivity of the substances. Meisenheimer and Caspar [28] therefore propose to regard them as complex compounds of magnesium in which the central atom has the co-ordination number 4, thus : $\mathrm{^{Et_2O}_{Et_2O}\!\!>\!\!Mg\!\!<\!\!^{Alk}_{Hal}}$. In this formula the alkyl group and halogen atom are united to the magnesium by main valencies, the ether molecules by subsidiary valencies. When brought into contact with acetone, etc., the latter, by virtue of its greater reaction energy, displaces a molecule of ether, yielding the substance $\mathrm{^{Me_2CO}_{Et_2O}\!\!>\!\!Mg\!\!<\!\!^{Alk}_{Hal}}$. It is suggested that re-arrangement of the bonds within the complex then occurs by which the subsidiary bond between the magnesium and the carbonyl oxygen becomes a chief bond; the alkyl group which has thus become detached from the magnesium atom attaches itself to the chief bond of the carbonyl carbon atom which has simultaneously become free, and the vacant co-ordination position of the magnesium atom is taken by a molecule of ether, thus : $\mathrm{^{Me_2CAlk\cdot O}_{Et_2O}\!\!>\!\!Mg\!\!<\!\!^{OEt_2}_{Hal}}$. This conception is in complete harmony with the observation of Ahrens and Stapler [28a] that magnesium bromide and iodide form dietherates from which one molecule of ether can be displaced readily by a molecule of aldehyde, ketone, or amine. It also explains the peculiar behaviour of allyl haloids towards magnesium; as the final product of these reactions, a crystalline mass is obtained which consists entirely of the magnesium haloid dietherate, the allyl radicle being quantitatively contained in the ethereal solution in the form of diallyl. The course of the reaction is explained as follows : The primary reaction consists in the formation of a normal Grignard compound, $\mathrm{^{Et_2O}_{Et_2O}\!\!>\!\!Mg\!\!<\!\!^{C_3H_5}_{Br}}$, from which a molecule of ether is immediately displaced by a further molecule of allyl bromide,

[28] Ber., 1921, 54, [B], 1655; A., i, 654.   [28a] A., 1905, i, 868.

$$\underset{C_3H_5Br}{Et_2O} \diagdown Mg \diagup\underset{Br}{C_3H_5}.$$ In this complex, the allyl residue of the alkyl haloid is only loosely attached by reason of the union of the bromine atom to the magnesium, which may be thus expressed :

$$C_3H_5\left[\underset{Br}{Et_2O} \diagdown Mg \diagup\underset{Br}{C_3H_5}\right].$$ As a consequence, when two such molecules come within range of one another, the allyl residue is readily detached, yielding diallyl. Simultaneously, a change in bonds occurs by which the second bromine atom becomes attached by a main valency to the magnesium atom and the diallyl group by a subsidiary valency. A hydrocarbon such as diallyl has, however, but little free valency, and is therefore readily displaced by the ether, thus giving a magnesium haloid dietherate. The peculiar property of allyl haloids is due to the reactivity of the halogen atom in these compounds and the relatively large amount of the available valency of the halogen atom. It is to be expected further that allyl bromide would have the same power of displacing ether from any similarly constituted Grignard compound. This is shown to be the case, since allyl bromide is found to react with ethereal solutions of magnesium methyl, ethyl, or phenyl bromide to give the magnesium haloid dietherate, and butene, pentene, and allylbenzene respectively.

The catalytic activity of ether and tertiary amines in promoting the action between magnesium and alkyl haloids cannot be explained satisfactorily by the assumption of the formation of oxonium salts of the type $\underset{Et}{Et} > O < \underset{I}{Me}$, since in this case a mixture of magnesium methyl and ethyl iodides must result. This difficulty is overcome by considering that the action between ether or base and alkyl haloid proceeds only to the subsidiary valency stage, $\underset{Et}{Et} > O \cdots MeI$, $Alk_3N \cdots PhI$, which accounts thus for the unusual mobility of the halogen atom.

The reducing action of the Grignard reagent under some conditions is assumed by K. Hess and H. Rheinboldt [29] to be due to magnesium hydrogen haloid. These authors also represent these reagents by co-ordination formulæ. They show that, under the conditions customary in the preparation of Grignard's reagents, magnesium does not react with gaseous hydrogen chloride in the presence of ether or benzene. Liquid hydriodic acid does not attack magnesium, whereas in the presence of dry ether a reaction occurs readily which, however, is due to the ready conversion of ether into ethyl iodide by hydrogen iodide. To avoid complications of this type, the " individual " Grignard compounds were used, when it was found that

[29] *Ber.*, 1921, **54**, [*B*], 2043; *A.*, i, 777.

magnesium ethyl iodide does not react with gaseous or liquid hydrogen iodide, alone or in the presence of benzene, whereas it is decomposed completely by hydrogen chloride with the liberation of ethane. Attempts to demonstrate the unaltered nature of the magnesium ethyl iodide after treatment with hydrogen iodide by bringing it into reaction with benzaldehyde led to the rather surprising isolation of benzyl alcohol instead of the expected phenylethylcarbinol. A similar result was observed with untreated magnesium ethyl iodide in warm benzene and, but to a less extent, in warm ether, whereas phenylethylcarbinol was exclusively obtained in ethereal solution at the atmospheric temperature.

According to these authors, the Grignard compounds can be represented most accurately by co-ordination formulæ, as, for example, $RR'C\!:\!O\text{---}Mg\!<^{Br}_{CH_2\cdot CH_3}$, and the reductions then occur in accordance with the scheme :

$$Mg\!<^{X}_{OH} + {^R_{R'}}\!\!>\!C\!<^{OH}_{CH_2\cdot CH_3} \underset{+H_2O}{\overset{\text{in the cold}}{\longleftarrow}} {^R_{R'}}\!\!>\!C\!:\!O\text{---}Mg\!<^{X}_{CH_2\cdot CH_3}$$

$$\overset{\text{warmed}}{\longrightarrow} {^R_{R'}}\!\!>\!C\!:\!O\text{---}Mg\!<^{X}_{H} + {^{CH_2}_{CH_2}} \overset{+H_2O}{\longrightarrow} {^R_{R'}}\!\!>\!C\!<^{OH}_{H} + Mg\!<^{X}_{OH}.$$
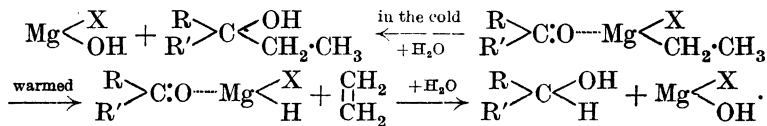
Since it is shown that the subsidiary reaction may be made into the main change by increasing the temperature, it is possible that a method is opened out for the reduction of substances containing the ketonic group and other reducible groups (for example, ethylenic linkings) which are not changed by reduction of the ketonic group. In any case, it is demonstrated that the avoidance of subsidiary reactions in the case of the aliphatic alkyl haloids (except the methyl compounds) can only be secured by the avoidance of elevated temperature, except under perfectly definite conditions.

Catalytic Hydrogenation and Dehydrogenation.

During the last three years much attention has been devoted to finding a satisfactory explanation of the phenomena observed during the catalytic hydrogenation of unsaturated compounds, the activation of the catalysts, and the catalytic dehydrogenation of alcohols.

It is still an open question whether oxygen is necessary for the activation of hydrogenating catalysts, and most of the work recently published bears on this point.

In a series of papers by E. F. Armstrong and T. P. Hilditch,[30] the linear nature of the reaction–time curve, at least in the earlier

[30] *Proc. Roy. Soc.*, 1919, [A], **96**, 137, 322; *A.*, 1919, ii, 403; 1920, ii, 102; *ibid.*, 1920, [A], **97**, 259; **98**, 27; *A.*, 1920, ii, 422, 608; *ibid.*, 1921, [A], **99**, 490; *A.*, ii, 582 *et seq.*

stages of the reaction, for catalysis at solid surfaces is demonstrated and shown to compare with hydrolysis brought about by means of enzymes. These investigators conclude that unstable complexes of catalyst and unsaturated compound are formed which break down on addition of hydrogen to saturated compound and regenerated catalyst. By this means, they explain the fact that hydrogenation and dehydrogenation may proceed simultaneously, even at the optimum temperature for the former process. They have succeeded, by using the reacting compounds in the liquid state, in hydrogenating an unsaturated compound at the expense of a saturated compound, which thereby undergoes reduction. With reduced nickel as the catalyst, a mixture of *cyclo*hexanol and methyl cinnamate at 180° gave a certain amount of *cyclo*hexanone and methyl β-phenylpropionate; whilst a mixture of ethyl stearate and methyl cinnamate at 230° produced a small quantity of methyl β-phenylpropionate together with some ethyl oleate, although the amount of the latter was insufficient to enable the authors to determine whether it was the ordinary ($\Delta^{9:10}$) ethyl oleate or the ethyl *iso*oleate ($\Delta^{10:11 \text{ or } 11:12}$) described previously by Moore.[31]

Either copper or nickel may be used to hydrogenate acetaldehyde or to dehydrogenate ethyl alcohol. It is noteworthy that the presence of a trace of water inhibits the former and promotes the latter reaction. The apparent specific volume has been shown by these same investigators to influence the activity of a catalyst : that is to say, a bulky preparation of nickel, or one supported on an inert substance, such as kieselgühr, is more active catalytically than a more compact preparation, such as one formed by reduction of the fused oxide. From their numerical results, Armstrong and Hilditch deduce that the catalytic activity of nickel can be satisfactorily explained by a consideration of the surface exposed, and that it is unnecessary to postulate the presence of oxides of nickel in the catalyst.

They have also established that simple ethylenic compounds are hydrogenated, in presence of sufficient nickel, at rates which are in approximately exact proportion to the absolute pressure of the hydrogen. At extremely low concentrations of the catalyst, the increase in rate of hydrogenation becomes less than proportional to the increase in pressure, especially in the cases of multi-ethylenic compounds such as linolein or citral. On the other hand, the presence of a group in the organic compound which has affinity for nickel, but is not open to hydrogenation, causes the speed of hydrogenation to increase with abnormal rapidity as the hydrogen pressure is increased. Thus the relation between rate of action

[31] *J. Soc. Chem. Ind.*, 1919, **38**, 320T.

and hydrogen concentration is evidently governed by the type of organic compound present. These results harmonise completely with the view that the process is primarily conditioned by an association of the ethylenic linking with the catalyst, which is itself associated with hydrogen.

W. G. Palmer [32] has studied the activity of copper as a catalyst for the dehydrogenation of the lower aliphatic alcohols. He finds that, although electrolytic copper, both when pure and when alloyed with zinc, is catalytically inactive, copper prepared by reduction of its oxide promotes dehydrogenation, although its activity decreases with time. He concludes that the active material is copper in the cuprous form, that the inactivation is due to a slow change of these molecules into the more stable cupric form, and that oxides of copper play no part in the catalysis. The same author in conjunction with (Miss) D. M. Palmer [33] has investigated the reduction of ethylene to ethane with nickel as a catalyst. From their results they infer that a preliminary selective adsorption of hydrogen takes place on the catalyst : thermal contact with ethylene molecules then causes evaporation of hydrogen and any ethane formed, after which ethylene is adsorbed on the catalyst and a nearly steady state of reaction is attained.

Rosenmund, Zetzsche, and Heise [34] have developed a theory of the influencing of catalysts by small quantities of other substances. By the addition of minute amounts of suitable promoters or inhibitants they have been able to control the reduction of benzoyl chloride in the presence of palladium or palladinised barium sulphate in such a manner that the chief reaction product may be benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene. The regulating substances were chosen to contain an element of variable valency, among the more important being quinoline, xanthone, dimethylaniline, and particularly quinoline which had been heated with sulphur.

In addition to the reduction of benzoyl chloride, Rosenmund and Zetzsche have studied the dehydrogenation of alcohols in the liquid state.[35] All the metals used as catalysts were practically inactive, but addition of quinoline induced specific activity, especially in the cases of copper, nickel, and silver. The best yields of aldehydes are obtained by the catalytic oxidation of an equimolecular mixture of alcohol, quinoline, and m-dinitrobenzene in cumene solution in the presence of copper. Secondary alcohols can be similarly

[32] *Proc. Roy. Soc.*, 1920, [*A*], **98**, 13; *A.*, 1920, ii, 609.

[33] *Ibid.*, 1921, [*A*], **99**, 402; *A.*, ii, 541.

[34] *Ber.*, 1921, **54**, [*B*], 425, 638, 2038; *A.*, ii, 320, 392, 632.

[35] *Ibid.*, 1092, 2033; *A.*, ii, 393, 631.

oxidised to ketones, but tertiary alcohols are not attacked by this method.

The use of platinum and palladium both in the colloidal and in the spongy state for catalytic hydrogenation has been shown by Willstätter and Waldschmidt-Leitz [36] to depend on the presence of oxygen in the catalyst. According to their view, the catalyst functions alternately as a peroxide (with the metal bivalent) and as a combined hydride and peroxide (with the metal quadrivalent), thus effecting the transfer of hydrogen. By treating their metals in suspension in glacial acetic acid with hydrogen they have obtained inactive catalysts which, however, are easily reactivated by shaking with air. They consider that some, but not all, cases of catalyst poisoning during hydrogenation are due to the gradual removal of the oxygen necessary for catalysis.

Similar results were found in the case of nickel : the lower oxides were catalytically active, but the pure metal, free from oxygen, was inactive until primed with a small quantity of air. Kelber,[37] however, carrying out hydrogenations at laboratory temperature, has been unable to confirm these observations in the case of nickel reduced from the carbonate and from the oxalate via the oxide, and has found that his catalyst becomes inactive when shaken with oxygen, and that treatment with hydrogen at 70—80° is then necessary to reactivate it. It seems only fair, however, to point out that Kelber's work was done with sodium cinnamate, whereas Willstätter and Waldschmidt-Leitz used a far greater variety of substances, including benzene, *cyclo*hexene, limonene, pyrrole, phthalic anhydride, *o*-benzylbenzoic acid, and *o*-naphthoylbenzoic acid.

Willstätter and Waldschmidt-Leitz divide unsaturated compounds into three classes, according to the ease with which they are hydrogenated : (*a*) ethylenic substances, which are reduced so rapidly that the rate of loss of oxygen from the catalyst is negligible in comparison; (*b*) simple aromatic compounds, which are hydrogenated with much less speed than the olefines, so that loss of oxygen, especially from small amounts of catalyst, may have a marked retarding effect on the velocity of hydrogenation; and (*c*) other substances, such as polynuclear aromatic compounds, the rate of hydrogenation of which is so small that deoxygenation of the catalyst occurs long before the hydrogenation is complete. In cases of this type, they recommend activation of the catalyst by priming with oxygen from time to time, as suggested by Willstätter and Jaquet.[38]

[36] *Ber.*, 1921, **54**, [*B*], 113; *A.*, ii, 185.   [37] *Ibid.*, 1701; *A.*, ii, 630.
[38] *Ibid.*, 1918, **51**, 767; *A.*, 1918, i, 391.

The application of the Nernst heat theorem, using the approximation formula, to the equilibria acetaldehyde, hydrogen, ethyl alcohol; and acetone, hydrogen, *iso*propyl alcohol, has been carried out by E. K. Rideal,[39] who confirms Sabatier's results that nearly complete hydrogenation or dehydrogenation can occur within the small temperature range from 100—350°.

E. B. Maxted,[40] using platinum and palladium as catalysts for the hydrogenation of oleic acid, has shown that the decrease in activity caused by the poisons lead, mercury, sulphur, arsenic, and zinc is, within the limits zero concentration of the inhibitant nearly to the concentration producing complete inactivation, directly proportional to the concentration of the inhibitant. He has already shown [41] that the occlusive power of palladium for hydrogen varies directly as the content of inhibitant (hydrogen sulphide in this case), so that it follows that the occlusive power for hydrogen varies directly as the catalytic activity. This result he has experimentally demonstrated for catalytic palladium poisoned by lead and using oleic acid as before.[42] He notes, however, that although the catalytic activity and occlusive power vary lineally with the concentration of the poison, the former property is much more susceptible to poisoning than the latter. In explanation of this, he suggests that whilst catalytic power is mainly a function of surface exposed, occlusion is not confined to the surface.

Carbohydrates.

Much activity has been displayed in the investigation of the carbohydrates, and the long series of researches by Purdie, Irvine, and other workers in the St. Andrews school on the simpler hexoses and their methylated derivatives have paved the way to an understanding of the constitution of some of the more complex members of this group of compounds. The general procedure of fully methylating the complex compound by means of methyl sulphate and sodium hydroxide, followed by methyl iodide and silver oxide, and then of hydrolysing the methylated compounds in which the hydroxyl groups are thus protected, has in several instances proved very successful, inasmuch as the properties of the methylated hexoses which are obtained on hydrolysis are fairly well known. This method is being widely adopted by other workers, and yields more certain results than the investigation of the acyl derivatives

[39] *Proc. Roy. Soc.*, 1921, [A], **99**, 153; A., i, 389.
[40] *T.*, 1920, **117**, 1501; 1921, **119**, 225.
[41] *Ibid.*, 1919, **115**, 1050; 1920, **117**, 1280.
[42] *Ibid.*, 1921, **119**, 1280.

of the sugars [43] or the acetolysis [44] of polysaccharides by acetyl bromide in the presence of hydrogen bromide and acetic acid, a complex reagent which brings about simultaneous acetylation, hydrolysis, and bromination. Haworth and Hirst [45] have fully methylated cellobiose, which they obtain in about 30 per cent. yield from cellulose by an improved method of acetolysis. This octamethyl derivative is shown to be heptamethylmethylcello-bioside, and splits up on hydrolysis into known butylene-oxidic forms of tetramethyl and trimethyl glucose.

The formula (I) for cellobiose which Haworth and Miss Leitch [46]

$$
\begin{array}{cc}
\text{(I.)} & \text{(II.)}
\end{array}
$$
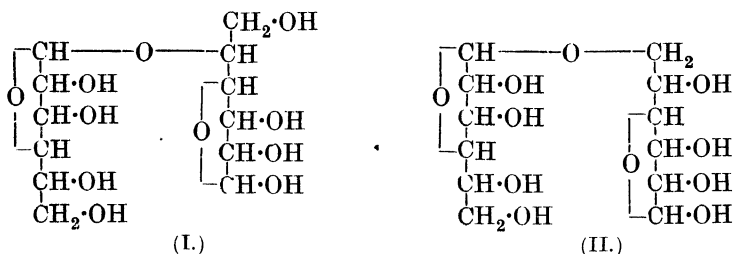
suggested during their research on maltose (II) has thus been confirmed.

The constitution of glucal,[47] which was discussed in last year's Report, has been fully proved and compounds of the type of glucal, $OH \cdot CH_2 \cdot CH(OH) \cdot CH \cdot CH(OH) \cdot CH \vdots CH$, have been prepared from other sugars. The names of these, such as rhamnal, lactal, cellobial, etc., have lost their significance as the compounds, when pure, have no aldehydic properties. Glucal itself is oxidised by perbenzoic acid to anhydromannose, which, with alcohol and water, yields mannose and ethylmannoside.

Analogous results have been obtained with rhamnal and cellobial, which incidentally confirm Haworth's formula for cellobiose.

It will be recalled that last year Irvine and Soutar [48] showed that the yield of pure glucose obtainable from cotton cellulose was, as a minimum, 85 per cent. of the theoretical amount calculated on the basis of the equation $(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6$. Further work by Monier-Williams [49] has increased the yield of crystalline glucose to more than 90 per cent. and affords strong, although not conclusive, evidence that the molecular unit of unmodified cellulose consists entirely of condensed glucose residues.

[43] K. Hess and E. Messmer, *Ber.*, 1921, **54**, [B], 499; *A.*, i, 305.

[44] M. Bergmann and F. Beck, *ibid.*, 1574; *A.*, i, 649.

[45] *T.*, 1921, **119**, 193.   [46] *Ibid.*, 1919, **115**, 809.

[47] M. Bergmann and H. Schotte, *Ber.*, 1921, **54**, [B], 440; *A.*, i, 307.

[48] *T.*, 1920, **117**, 1489.   [49] *Ibid.*, 1921, **119**, 803.

It has been known for some years that when cellulose or starch is subjected to dry distillation under reduced pressure a well-defined, crystalline compound can be isolated. This was termed by Pictet, its discoverer, *l*-glucosan, and he has argued [50] that the formula of this anhydro-glucose must afford a clue to the constitution of cellulose and starch, on the assumption that these are polymerides of *l*-glucosan. Now W. S. Denham [51] has shown that the limit of methylation of cellulose is practically that required for the formation of trimethyl cellulose, which gives on hydrolysis the same trimethyl glucose isolated by Haworth and Hirst [52] from the products of hydrolysis of methylated cellobiose.

The importance, therefore, of ascertaining the constitution of *l*-glucosan is apparent, and Irvine and Oldham [53] have been successful in converting it into a trimethyl glucose identical with that obtained previously from methylglucoside and from maltose, and quite distinct from that obtained (as described above) in two ways from cellulose. It is, however, scarcely a matter of surprise that, considering the complex changes undergone by carbohydrates on heating, the constitution of *l*-glucosan bears no structural relation to that of cellulose. In fact, it has thus been proved that *l*-glucosan is 1 : 6-β-glucose anhydride, and would be designated more correctly as β-glucosan.
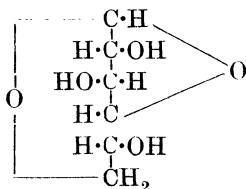
Some progress can be recorded in the elucidation of the constitution of starch and the first products of its hydrolysis. The crystalline dextrins first obtained by Schardinger [54] in 1903 by the action of certain bacteria (notably *Bacillus macerans*) were investigated by Pringsheim [55] and characterised as diamylose $(C_6H_{10}O_5)_2$, triamylose, tetra-amylose, hexa- and octa-amylose, the molecular weights of the acetyl derivatives of these being determined in several solvents. These compounds have been recently investigated further by Karrer [56] and his co-workers, who have subjected them to the action of acetyl bromide and acetic acid. In this way,

[50] Inter alia, *Helv. Chim. Acta*, 1918, **1**, 187.
[51] *T.*, 1921, **119**, 77.   [52] *loc. cit.*   [53] *T.*, 1921, **119**, 1744.
[54] *Zeit. Nahr. Genussm.*, 1903, **6**, 865; *A.*, 1904, ii, 67.
[55] *Ber.*, 1913, **46**, 2959; *A.*, 1913, i, 1156.
[56] *Helv. Chim. Acta*, 1921, **4**, 169, 678; *A.*, i, 310, 768.

the so-called α-tetra-amylose is converted first into acetylated α-diamylose and then by the opening of the anhydride ring quantitatively into aceto-bromomaltose. It would thus seem that α-amylose is the first known anhydride of a disaccharide.

The methylation of potato starch has been carried out also by Karrer.[57] The product obtained by the use of methyl sulphate and baryta water has the empirical formula $[C_6H_8O_3(OMe)_2]_n$ with a molecular weight of about 1100, and can be further methylated by means of silver oxide and methyl iodide, giving a methylostarch having a molecular weight in water of about 1200. Solutions of the methylated starch in water or chloroform exhibit the Tyndall effect and under the ultramicroscope show colloidal particles. The aqueous solutions, however, readily undergo ultrafiltration with little loss, and the filtrates appear optically empty and present no Tyndall effect. The size of the starch molecule has not yet been determined and it appears certain that it is much smaller than has been freely suggested by the older workers.

Nitrogen Compounds.

It has been known for some time that an aldehyde in the presence of ammonia can be oxidised to the amide of the corresponding acid. Mignonac [58] has now shown that alcoholic solutions of aldehydes and ketones can be reduced by hydrogen in the presence of a nickel catalyst to the corresponding amine in accordance with the general scheme, $R \cdot CHO + NH_3 \longrightarrow R \cdot CH(OH) \cdot NH_2 \longrightarrow R \cdot CH_2 \cdot NH_2$. The reaction appears to be general and possesses the advantage over other methods for the preparation of primary amines in that there is no simultaneous formation of secondary and tertiary amines.

The reaction between secondary bases, formaldehyde, and alcohols or mercaptans has been studied by C. M. McLeod and Mrs. G. M. Robinson.[59] These authors show that the reaction $NHR_2 + CH_2O + R'OH(\text{or } R'SH) \longrightarrow R_2N \cdot CH_2 \cdot OR' + H_2O$ is quite general; the resulting dialkylaminomethyl alkyl ethers and sulphides, which are best obtained by condensing the components in the cold in the presence of an excess of potassium carbonate, are mobile oils which distil without decomposition. The thio-ethers are more stable than the ethers, but all are more or less readily hydrolysed by water and acids.

Up to the present, methods for the reduction of amino-acids

[57] *Helv. Chim. Acta*, 1920, **3**, 620; *A.*, 1920, i, 820; *ibid.*, 1921, **4**, 185, 263; *A.*, i, 311, 313.

[58] *Compt. rend.*, 1921, **172**, 223; *A.*, i, 165.　　　[59] *T.*, 1921, **119**, 1470.

with primary amino-groups to the corresponding amino-alcohols have not been available. It has now, however, been found [60] that the well-known method of Bouveault and Blanc, in which an ester is reduced with sodium and alcohol, gives, if applied to the acetylated esters of the amino-acids, good yields of the corresponding amino-alcohols. Most of the amino-alcohols thus obtained are now described for the first time and appear to be of considerable physiological interest.

Whilst the substitution of the imino-hydrogen in " saccharin " by alkyl groups entirely destroys the sweetness of that substance, the position is completely reversed in the case of diglycollimide,[61] which, although itself tasteless, yields alkylimides of the general formula $O{<}^{CH_2\cdot CO}_{CH_2\cdot CO}{>}NR$, which increase in sweetness with an increasing number of carbon atoms up to a maximum in the N-propyl derivative. The aryl derivatives, on the other hand, are almost tasteless. These cyclic imide-ethers of diglycollic acid are very hygroscopic and are of little practical importance as sweetening agents, as they are slowly hydrolysed by the absorbed water to the corresponding alkylamine hydrogen diglycollates.

ROBERT H. PICKARD.

. PART II.—HOMOCYCLIC DIVISION.

Reactions.

Reduction.—It is remarkable that the catalytic hydrogenation of ω-trifluorotoluene, $Ph\cdot CF_3$, should lead exclusively to the production of trifluoromethyl*cyclo*hexane, whilst under similar conditions α-difluorotoluene yields difluoromethyl*cyclo*hexane together with a small proportion of methyl*cyclo*hexane.[1] This stability of fluorine in a side chain towards molecular hydrogen in presence of platinum black is in sharp contrast to the ready removal of the same substituent when attached to the aromatic nucleus, since p-fluorobenzoic acid gives first benzoic acid and then *cyclo*hexanecarboxylic acid.

Ethyl α-naphthoate is reduced by sodium and alcohol to a methyl-dihydronaphthalene,[2] and this reaction recalls the fact that saturated acids can occasionally be reduced to hydrocarbons containing the same number of carbon atoms by means of hydriodic acid and

[60] P. Karrer, W. Karrer, H. Thomann, E. Horlacher, and W. Mäder, *Helv. Chim. Acta*, 1921, **4**, 76; *A.*, i, 228.

[61] M. Sido, *Ber. deut. Pharm.Ges.*, 1921, **31**, 118; *A.*, i, 447.

[1] F. Swarts, *Bull. Acad. roy. Belg.*, 1920, 399; *A.*, i, 657.

[2] H. de Pommereau, *Compt. rend.*, 1921, **172**, 1503; *A.*, 1921, i, 567.

phosphorus. Undecane, for example, may be obtained in this manner from undecoic acid.[3] A device likely to prove useful in many cases is that employed for the reduction of nitropiperonal, which can be effected if the aldehyde group is first protected by condensation with *p*-toluidine and the reduction performed in aqueous alcoholic solution by means of sodium sulphide. The aminoazomethine derivative obtained in this way is then readily hydrolysed by hot water.[4] An important addition to the methods available for the preparation of arylhydroxylamines consists in the reduction of nitro-compounds in emulsified suspension by means of sodium sulphide.[5] The process is a modification of that of Willstätter and Kubli,[6] and the essential novel features are the replacement of ammonium sulphide by sodium sulphide, the employment of aqueous instead of alcoholic solutions, and the production of an emulsion, facilitated by the addition of small amounts of calcium chloride.

Oxidation.—The behaviour of sodium phenoxide at 485—490° in an atmosphere of hydrogen or nitrogen has been examined [7] and the products are hydrogen, methane or ethane, benzene, diphenyl, diphenyl oxide, 2-hydroxydiphenyl, and larger relative amounts of four dihydroxydiphenyls (2 : 2′-, 3 : 3′-, 3 : 4′-, and probably 2 : 3′-).

Novel results have been obtained in an extensive study of the action of hydrogen peroxide in alkaline solution on unsaturated ketones.[8] In most cases, the product is an ethylene oxide derivative containing one atom of oxygen more than the original ketone. Thus styryl methyl ketone yields β-acetyl-α-phenylethylene oxide (I), m. p. 52—53°, together with a liquid isomeride, and the nature of these substances is placed beyond doubt by the fact that the corresponding compound (II) from phenyl styryl ketone is identical with the product obtained by Widman [9] by the action of benzaldehyde on ω-bromoacetophenone.

$$O<\genfrac{}{}{0pt}{}{CHPh}{CHAc} \qquad\qquad O<\genfrac{}{}{0pt}{}{CHPh}{CHBz}$$

(I.) \qquad\qquad\qquad\qquad (II.)
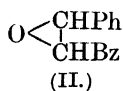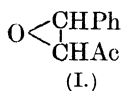
These oxides liberate iodine from potassium iodide and acetic acid with regeneration of the unsaturated ketone, and the compound

[3] Krafft, *Ber.*, 1882, **15**, 1697.

[4] A. Rilliet and L. Kreitmann, *Helv. Chim. Acta*, 1921, **4**, 588; *A.*, i, 567.

[5] A. Lapworth and (Mrs.) L. K. Pearson, *T.*, 1921, **119**, 765, 768.

[6] *Ber.*, 1908, **41**, 1936.

[7] F. Hofmann and M. Heyn, *Brennstoff-Chem.*, 1921, **2**, 147; *A.*, i, 506.

[8] E. Weitz and A. Scheffer, *Ber.*, 1921, **54**, [*B*], 2344; *A.*, i, 869; *ibid.*, 2327; *A.*, i, 868.

[9] *A.*, 1913, i, 1220.

(I) is transformed by hydrogen chloride in acetic acid into an oily chlorohydrin which slowly liberates hydrogen chloride, with formation of hydroxymethylenebenzyl methyl ketone, OH·CH:CPh·COMe.

Halogenation.—A comparison [10] of the activity of catalysts in the chlorination of benzene by sulphuryl chloride has shown that anhydrous aluminium chloride is by far the most efficient, the yield of monochlorobenzene amounting to nearly 90 per cent. of the theory in some experiments.

It is, perhaps, a little remarkable that the dibromination of ethylbenzene should lead to αβ-dibromoethylbenzene,[11] which, by the action of magnesium, is converted into styrene.

Etherification and Esterification.—The very useful process of etherification of phenols by means of arylsulphonic esters has been examined in detail so as to determine the optimal conditions,[12] and workers who have occasion to alkylate phenolic bases especially should make themselves familiar with the results. The preparation of many benzyl derivatives, benzyl esters, ethers, phenylacetonitrile, benzylamines, etc., is found to proceed in aqueous solution so as to give far higher yields than those obtained in other ways.[13]

Replacement of Substituents in Aromatic Compounds.—Improvements have been made in the already numerous processes for the replacement of halogen in benzene and naphthalene derivatives by hydroxyl.[14] It is found that the salt of a weak acid can often replace the alkali usually employed; thus an 83 per cent. yield of salicylic acid is obtained when potassium *o*-chlorobenzoate is heated with water, sodium acetate, and a trace of cupric acetate at 140—150°. Partly successful attempts have been made to apply similar reactions to the replacement of halogens by sulphur and selenium and by the sulphonic and arsinic acid groups.

Thionbenzoyl Derivatives.—The only known substance containing the group ·CSCl is thiocarbonyl chloride, and special interest attaches, therefore, to the preparation [15] of thionbenzoyl chloride, Ph·CSCl, which may be obtained as a reddish-violet, mobile liquid, b. p. 60—62°/0·2 mm., of disagreeable odour, by the action of thionyl chloride on dithiobenzoic acid. The substance behaves as a true acid chloride, yielding an anilide and methyl thionbenzoate, Ph·CS·OMe, by the action of aniline and methyl alcohol respectively. For comparison, the isomeric methyl thiobenzoate, Ph·CO·SMe, was prepared from benzoyl chloride and methyl mercaptan. Thion-

[10] O. Silberrad, *T.*, 1921, **119**, 2029.

[11] J. von Braun and K. Moldanke, *Ber.*, 1921, **54**, [B], 618; *A.*, i, 405.

[12] Z. Földi, *Ber.*, 1920, **53**, [B], 1839; *A.*, 1920, i, 877.

[13] M. Gomberg and C. C. Buchler, *J. Amer. Chem. Soc.*, 1920, **42**, 2059; *A.*, 1920, i, 839.

[14] K. W. Rosenmund and H. Harms, *Ber.*, 1920, **53**, [B], 2226; *A.*, i, 103.

[15] H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 824; *A.*, i, 25.

benzoyl chloride yields benzoyl chloride and monoclinic sulphur when heated at 110—120° in a current of oxygen.

Diazonium Salts.—The researches of Meldola and others have made us familiar with the fact that a diazo-group has a loosening effect on ortho-substituents, and that this property is much enhanced when there is a positive [16] group situated in the ortho- or para-position with respect to the affected radicle. Thus the diazotisation of dinitroanilines ($NH_2 : NO_2 : NO_2 = 1 : 2 : 3$ or $1 : 2 : 5$) frequently leads to the formation of diazo-oxides. Numerous methods have been suggested with the object of avoiding this difficulty, and the latest device,[17] which apparently works well, is to diazotise the feeble base in acetic acid solution at a low temperature with a solution of sodium nitrite in sulphuric acid monohydrate. Even $2 : 4 : 6$-trinitroaniline can be diazotised and $2 : 4 : 6$-trinitro-*m*-phenylenediamine tetrazotised by this method. The $2 : 4 : 6$-trinitrobenzenediazonium salt is unusually reactive and couples with mesitylene to form $2 : 4 : 6$-trinitrobenzeneazomesitylene, $C_6H_2(NO_2)_3 \cdot N_2 \cdot C_6H_2Me_3$,[18] which may be reduced to mesidine.

A curious reaction which may be employed for the preparation of the arylsulphinic acids and aromatic azoimides occurs when, for example, benzenediazonium chloride is allowed to react with an alkaline solution of *p*-toluenesulphonamide.[19] The process is a fairly general one, results in high yields, and may be carried out in accordance with either of the equations (1) or (2) :

$$R \cdot SO_2 \cdot NH_2 + R'N_2Cl = R \cdot SO_2H + R'N_3 + HCl \quad . \quad . \quad . \quad (1)$$
$$R \cdot SO_2 \cdot NH_2 + 2R'N_2Cl = R \cdot SO_2 \cdot N_2 \cdot R' + R'N_3 + 2HCl \quad . \quad (2)$$
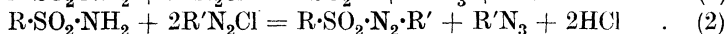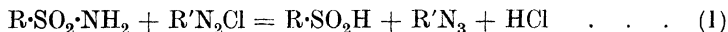
Hydrazine Derivatives.—Sodium hyposulphite gives excellent results in the reduction of diazo-salts, and *p*-nitrophenylhydrazine may be prepared in this way from *p*-nitroaniline in a yield amounting to 95 per cent. of the theoretical.[20] The action of azodicarboxylic ester on β-naphthylamine leads to the production of 2-amino-1-dicarbethoxyhydrazinonaphthalene,[21]

$$N(CO_2Et) \cdot NH \cdot CO_2Et$$

---
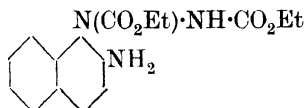
[16] By this term are implied the groups like $-NO_2$, $-CO_2H$, $-SO_2H$, etc., usually called negative. Their true character as positive groups has in recent years been emphasised by Fry, Lapworth, Vorländer, and others. It is true that such groups have a negative effect on the atom to which they are united.

[17] E. Misslin, *Helv. Chim. Acta*, 1920, **3**, 626; *A.*, 1920, i, 887.

[18] K. H. Meyer and H. Tochtermann, *Ber.*, 1921, **54**, [B], 2283; *A.*, i, 895.

[19] P. K. Dutt, H. R. Whitehead, and A. Wormall, *T.*, 1921, **119**, 2088.

[20] L. Thomson, *J. Soc. Dyers and Col.*, 1921, **37**, 7; *A.*, i, 133.

[21] O. Diels, *Ber.*, 1921, **54**, [B], 213; *A.*, i, 280.

Condensations.—The condensation of acetylene with benzene in presence of aluminium chloride gives αα-diphenylethane and 9 : 10-dimethylanthracene hydride in approximately equal proportions, along with traces of styrene.[22] Toluene gives *as*-di-*p*-tolylethane, 2 : 7-dimethylanthracene, and smaller relative amounts of 2 : 6-dimethylanthracene, β-methylanthracene, xylene, mesitylene, and ψ-cumene. Chlorobenzene gives as chief product di-*p*-chloro-*s*-diphenylethane, $C_6H_4Cl \cdot CH_2 \cdot CH_2 \cdot C_6H_4Cl$.

Nitriles are increasingly employed for the synthesis of phenolic ketones, and a whole series of acyl resorcinols and phloroglucinols has been prepared [23] by condensing the phenols with aliphatic nitriles according to the method devised by Hoesch.[24] These substances are remedies against the tape-worm; the resorcinol derivatives are as useful as those derived from phloroglucinol, and the most valuable acid residue appears to be *iso*hexoyl. A mixture of cyanogen and hydrogen chloride reacts as the dichlorodi-imide of oxalic acid, and with resorcinol in ethereal solution condenses to products which yield resorcylglyoxylic acid, $C_6H_3(OH)_2 \cdot CO \cdot CO_2H$, and 2 : 4 : 2' : 4'-tetrahydroxybenzil, $C_6H_3(OH)_2 \cdot CO \cdot CO \cdot C_6H_3(OH)_2$, along with other substances on hydrolysis.[25] Orcinol gives only the glyoxylic acid derivative.

Benzanilideiminochloride and its derivatives substituted in the nucleus condense readily with resorcinol, apparently in accordance with the scheme :—

$$C_6H_4(OH)_2 + CPhCl{:}NPh \longrightarrow C_6H_4(OH) \cdot O \cdot CPh{:}NPh + HCl$$

$$C_6H_3(OH)_2 \cdot CPh{:}NPh.$$
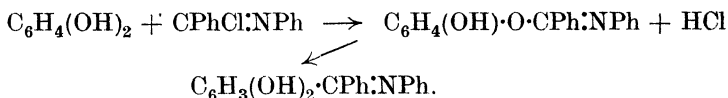
The first reaction occurs at 100° and the isomeric change at about 150°, the final product being readily hydrolysed by dilute hydrochloric acid with formation of benzoresorcinol.[26] This process is analogous to Hoesch's synthesis and also to Dimroth's preparation of β-resorcylaldehyde by the hydrolysis of the anilide resulting from the interaction of resorcinol, formanilide, and phosphoryl chloride in ethereal solution.[27] The latter method has now been applied with good results to the preparation of alkylaminobenzophenones, replacing the resorcinol by a tertiary amine and the formanilide by a benzanilide.[28] The substances formerly described by other

[22] O. W. Cook and V. J. Chambers, *J. Amer. Chem. Soc.*, 1921, **43**, 334; *A.*, i, 332.

[23] P. Karrer and S. Rosenfeld, *Helv. Chim. Acta*, 1921, **4**, 707; *A.*, i, 793.

[24] *Ber.*, 1915, **48**, 1122.

[25] P. Karrer and J. Ferla, *Helv. Chim. Acta*, 1921, **4**, 203; *A.*, i, 341.

[26] H. Stephen, *T.*, 1920, **117**, 1529.

[27] Dimroth, Zöppritz, *Ber.*, 1902, **35**, 995.

[28] J. Meisenheimer, E. von Budkewicz, and G. Kananow, *Annalen*, 1921, **423**, 75; *A.*, i, 356.

authors as dialkylaminobenzophenones are actually benzanilides. Dimethylaminobenzophenone has been employed for the preparation of leucotriphenylmethane dyes of the type RR_1R_2CH in the hope of resolving some member of the class and determining the question of the survival or disappearance of optical activity after oxidation and subsequent reduction. Racemisation is certainly to be anticipated.

The Transformations of Arylhydroxylamines.—It is impossible adequately to discuss in this Report the voluminous experimental work of Bamberger [29] on this subject, but some reference at least is necessary to the careful comparison drawn between the behaviour of an arylhydroxylamine and the corresponding arylazide towards sulphuric acid under various conditions. The results are closely parallel with the significant exception that azoxy-compounds, frequently obtained from the hydroxylamines, are never produced from the azides. This disposes of the suggestion which has been put forward [30] that the parallelism is due to preliminary conversion of the azide into the hydroxylamine by loss of nitrogen and hydration. Bamberger considers that the transformations are best explained by the formation of an arylimide, $Ar-N<$, from the hydroxylamine by loss of water and from the azide by loss of nitrogen. The formation of aminophenol then occurs as follows :—
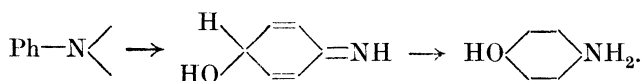
One further example may be illustrated, the conversion of *m*-xylylazide into 2-amino-*p*-5-xylenol :—
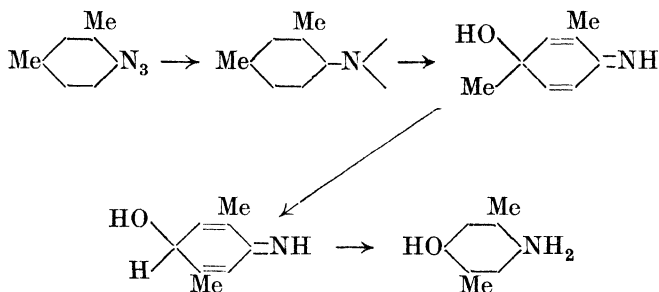
Of the numerous further reactions, reduction leads to aniline derivatives and hydrolysis to dihydroxybenzenes, reduction and hydrolysis to phenol derivatives. The arylimide may also add on

[29] *J. pr. Chem.*, 1921, [ii], **102**, 267; *A.*, i, 716; *Annalen*, 1921, **424**, 233; *A.*, i, 716; *ibid.*, 297; *A.*, i, 723.

[30] Friedländer and Zeitlin, *A.*, 1894, i, 184.

an alcohol, resulting in the production of phenolic ethers. The somewhat more complex problem of the changes induced by halogen acids is also discussed.

Substitution and Orientation.

The nitration of benzotrichloride to m-nitrobenzotrichloride was referred to in the Report for the year 1919, and it is now found that the very stable ω-trifluorotoluene also yields on nitration the m-nitro-derivative as chief product.[31] These results are in agreement with the principle of induced latent polarity of atoms in a chain which was also discussed in the Report for the year 1919.

The examination [32] of the nitration and chlorination of 2-chloro-p-toluenesulphonyl chloride has given results which may be summarised in the scheme :—
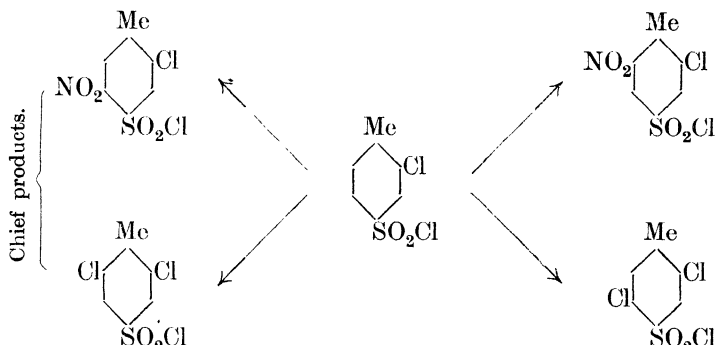
This may be compared with the behaviour of 4-nitroveratrole :—
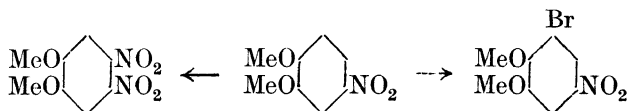
There is evidently a general tendency for the entrance of halogen to be definitely directed by positive groups to the meta-position to a greater extent than is the case when the entering substituent is nitroxyl.

The effect of chloro- and nitro-groups on the mobility of other similar substituents has been exhaustively investigated by Hollemann and his collaborators [33] in the case of the dichlorodinitro-

[31] F. Swarts, *Bull. Acad. roy. Belg.*, 1920, 389; *A.*, i, 656.

[32] W. Davies, *T.*, 1921, **119**, 853.

[33] A. F. Hollemann, A. I. den Hollander, and F. E. van Halften, *Rec. trav. chim.*, 1921, **40**, 323; *A.*, i, 503; A. F. Hollemann and F. E. van Haeften, *ibid.*, 67; *A.*, i, 167; E. J. E. Hüffer, *ibid.*, 451; *A.*, i, 549; A. F. Hollemann, *Rec. trav. chim.*, 1920, **39**, 736; *A.*, i, 102.

benzenes, the six trichloronitrobenzenes, the six trichlorodinitro-benzenes, the three tetrachlorobenzenes, pentachlorobenzene, and hexachlorobenzene. In general, the results obtained in studying the action of sodium methoxide are in harmony with previous experience, although some novel features are brought to light. Most interesting is the fact that the reactivity of a chlorine atom is enhanced by the entrance of a second chlorine atom in the meta-position. It will be recalled that Wieland and Sakellarios [34] showed that ethylene is capable of nitration to β-nitroethyl nitrate and, in correcting an earlier publication relating to the action of nitric acid on αα-diphenylethylene, Anschütz [35] discloses the interesting fact that Kekulé had in 1877 reached the opinion that nitroethyl nitrate is the product of the action of nitric acid on ethylene. The course of the nitration of diphenylethylene in glacial acetic acid solution is shown in the scheme :—

$$CPh_2{:}CH_2 \xrightarrow{+HNO_3} HO{\cdot}CPh_2{\cdot}CH_2{\cdot}NO_2 \xrightarrow{-H_2O} CPh_2{:}CH{\cdot}NO_2$$
$$\text{(III.)} \qquad\qquad\qquad \text{(IV.)}$$

$$CPh_2{:}CH{\cdot}NO_2 \xrightarrow{+HNO_3} HO{\cdot}CPh_2{\cdot}CH(NO_2)_2 \xrightarrow{-H_2O} CPh_2{:}C(NO_2)_2$$
$$\text{(V.)}$$
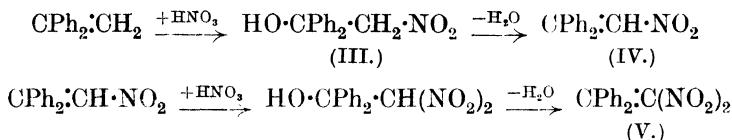
III, IV, and V are isolated and the latter undergoes reduction in the following manner :—

$$CPh_2{:}C(NO_2)_2 \rightarrow CPh_2{:}C(NH_2)_2 \rightarrow CPh_2{:}C{:}NH \rightarrow CHPh_2{\cdot}CN.$$
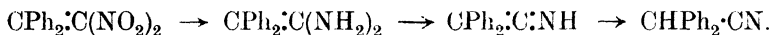
The nitration of ethylene derivatives has also been studied by Wieland [36] in continuation of his comprehensive researches. The substance (III) above is obtained by the action of a solution of absolute nitric acid in carbon tetrachloride on diphenylethylene at − 10°. In some cases the primary product cannot be isolated, thus the action of nitric acid on β-methyl-Δ^β-butylene, $CMe_2{:}CHMe$, leads immediately to the nitro-derivative, $CMe_2{:}CMe{\cdot}NO_2$, mixed with some nitroisoamyl nitrate.

These observations are, of course, extremely instructive in relation to the mechanism of substitution in aromatic compounds which by analogy are due to reactions of addition and fission. During the past year Kurt H. Meyer has emphasised the addition theory of diazo-coupling [37] and his views will meet with general support in most respects, but he appears to think that the gap in auxochromic or activating power existing between Me and OMe involves no necessity for a special explanation. Nevertheless, the existence of

[34] A., 1920, i, 280.

[35] Anschütz and Hilbert, Ber., 1921, **54**, [B], 1854 ; A., i, 783.

[36] H. Wieland and F. Rahn, ibid., 1770 ; A., i, 782.

[37] Ibid., 2265 ; A., i, 855.

conjugated ethylene–nitrogen and ethylene–oxygen systems can scarcely be disputed, and Meyer does not dispose of or even contemplate the possibility that the unsaturated system in phenols and amines includes the oxygen or nitrogen atoms.[38] This would, after all, be a mere extension of the assumption already made in order to explain ortho- and para-substitution by reference to the length of the unsaturated chain to which addition occurs.

Geometrical Isomerism.

A third monobromostyrene has been prepared,[39] and the isomerides are obtained by the following methods. (A), m. p. 6—7°, by heating sodium dibromo-β-phenylpropionate with an aqueous solution of sodium carbonate; (B), m. p. — 43°, by the action of hydrogen bromide on phenylacetylene; (C), m. p. — 8 to — 7°, by heating phenyl bromostyryl ketone, $CHPh:CBr\cdot COPh$, with powdered sodium hydroxide. A and C (the new isomeride) both give αββ-tribromoethylbenzene on bromination, whereas B gives ααβ-tribromoethylbenzene. A and C are therefore stereoisomerides of the formula $CHPh:CHBr$. Auto-oxidation of the substance B yields ω-bromoacetophenone as the result of an intramolecular rearrangement.[40] The two ω-bromostyrenes are very sensitive to light and either alone or mixed are converted to a substance or mixture with a constant melting point of 2°.[41]

Gentle isomerisation of safrole, $CH_2O_2:C_6H_3\cdot CH_2\cdot CH:CH_2$, by means of dilute alcoholic potassium hydroxide at 82—86° produces a new unstable *cis-iso*safrole, $CH_2O_2:C_6H_3\cdot CH:CH\cdot CH_3$, readily transformed by alkali at a higher temperature into the known *trans*-modification.[42] The isomerides can be interconverted through their dibromides and related monobromo*iso*safroles, the latter yielding the *iso*safroles on reduction with zinc and ethyl alcohol. It is stated that the *iso*safrole dibromides are optically active, but this must surely be an error, especially since safrole is always isolated from essential oils containing active constituents.

Formylphenylacetanilide, prepared from phenylacetanilide and formic ester by the action of sodium wire in ethereal suspension, has been isolated [43] in two forms, m. p. 68° and m. p. 98°, which are apparently not desmotropic, but the geometrical isomerides

---

[38] Since writing the above, a paper in the December number of the *Berichte* has been consulted, in which Auwers criticises the views of Meyer and points out that physical data strongly support the hypothesis of the existence in phenols of conjugated systems which include the oxygen atom.

[39] C. Dufraisse, *Compt. rend.*, 1920, **171**, 960; *A.*, i, 17.

[40] *Idem, ibid.*, 1921, **172**, 162; *A.*, i, 168.　　[41] *Idem, ibid.*, 1921, **11**, 83; *A.*, i, 104.

[42] Shoichiro Nagai, *J. Coll. Eng. Tokyo*, 1921, **11**, 83; *A.*, i, 857.

[43] W. Wislicenus and R. Erbe, *Annalen*, 1920, **431**, 119; *A.*, 1920, i, 841.

of the enol modification, $HO \cdot CH:CPh \cdot CO \cdot NHPh$. The related piperidides have also been prepared and exhibit a similar behaviour.

The formulæ VI and VII for saturated dimerides of cinnamic acid allow for the existence of eleven isomerides, five corresponding with VI and six with VII.

$$Ph \cdot \underset{|}{C}H \cdot \underset{|}{C}H \cdot CO_2H$$
$$CO_2H \cdot \underset{|}{C}H \cdot \underset{|}{C}H \cdot Ph$$
(VI.)

$$Ph \cdot \underset{|}{C}H \cdot \underset{|}{C}H \cdot CO_2H$$
$$Ph \cdot \underset{|}{C}H \cdot \underset{|}{C}H \cdot CO_2H$$
(VII.)
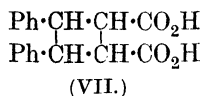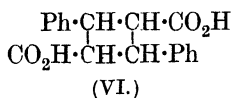
The isolation of a seventh truxillic acid [44] proves for the first time that these substances belong to both series depicted. It is proposed to term the dimerides of *trans*-cinnamic acid truxillic acids as formerly, and for those derived from *cis*-cinnamic acid the name truxinic acids is adopted. β-Truxinic acid, which itself results from the illumination of *cis*-cinnamic acid, yields the new isomeride, neotruxinic acid, by the prolonged action of aqueous pyridine at 160—170°. The acid has also been found to occur in small amount among the truxillic acids obtained during the preparation of cocaine.

In the tetrahydronaphthalene series, the method of condensation with acetone is found to distinguish between *cis*- and *trans*-diols, only the former giving dioxymethylene derivatives.[45] Nevertheless, the diagnostic value of the reaction has its limits, since both *cis*- and *trans*-1 : 2-*cyclo*heptanediols yield *iso*propylidene ethers.[46] The oxidation of *cyclo*heptene by means of potassium permanganate and magnesium sulphate yields *cis*-1 : 2-*cyclo*heptanediol, m. p. 46°, whilst the *trans*-compound, m. p. 63°, is obtained by the use of peroxybenzoic acid in chloroform solution followed by the action of dilute hydrochloric acid. An ingenious and novel device has been evolved [47] in order to determine the configurations of the two αα'-dibromoadipic acids, $CO_2H \cdot CHBr \cdot CH_2 \cdot CH_2 \cdot CHBr \cdot CO_2H$, m. p.'s 193° and 139°. The method is probably of general applicability, and depends on the replacement of the bromine atoms by a bivalent group so as to produce a ring. The product typified by the expression VIII will be obtained in the *cis*- or *trans*-modification according as the starting point is respectively the meso- or racemic form of the dibromo-acid, and if RH_2 is a symmetrical molecule, only the

[44] R. Stoermer and E. Laage, *Ber.*, 1921, **54**, [*B*], 77; *A.*, i, 179; R. Stoermer and F. Scholtz, *ibid.*, 85; *A.*, i, 180; R. Stoermer and E. Laage, *ibid.*, 96; *A.*, i, 182.

[45] J. Böeseken and H. G. Derx, *Rec. trav. chim.*, 1921, **40**, 519; *A.*, i, 663.

[46] *Idem*, *ibid.*, 529; *A.*, i, 663.

[47] W. H. Perkin and E. Robinson, *T.*, 1921, **119**, 1392.

trans-modification will be resolvable into optically active components,

$$\begin{matrix} CH_2 \cdot CH \cdot CO_2H \\ | \qquad >R \\ CH_2 \cdot CH \cdot CO_2H \end{matrix} \quad \text{(VIII).}$$
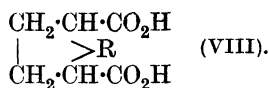
The diethyl ester of the dibromoadipic acid, m. p. 193°, is a readily purified solid and condenses with the sodium derivative of malonic ester to a tetracarboxylic ester which by the usual processes yields *cyclo*pentane-1 : 2 : 3-tricarboxylic acid. This substance could be resolved with the aid of brucine, and the acid, m. p. 193°, is therefore the racemic modification of dibromoadipic acid. In order to make the argument clear, all possible configurations of the *cyclo*pentanetricarboxylic acid are given below :

(IX.)

(X.)

(XI.)

(XII.)
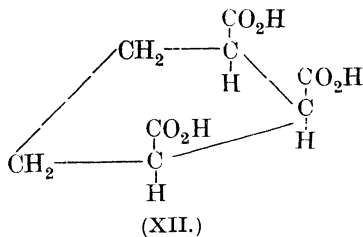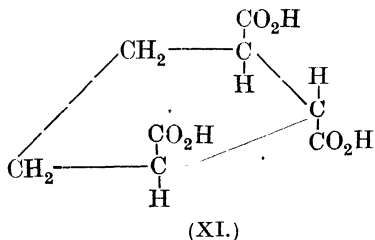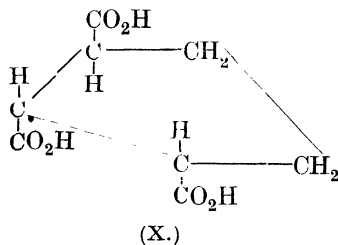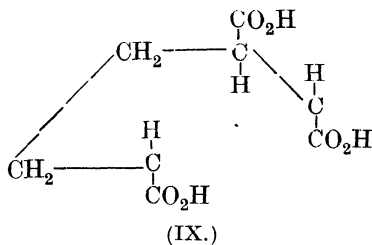
X is the mirror image of IX, whilst XI and XII have superposable mirror images. Consequently, the acid obtained as described above is the inactive mixture of IX and X, and reference to the models will show that these configurations are directly related to those of dextro- and lævo-αα'-dibromoadipic acid.

The existence of a peculiar form of isomerism in the diphenyl series, exemplified at present only in the case of the two *oo*-dinitrobenzidines and their derivatives,[48] has been confirmed by the isolation of two 6 : 6'-dinitrodiphenic acids.[49] The first isomeride, m. p. 297° or 303°, was already known and was obtained by Schulze [50]

[48] J. C. Cain, A. Coulthard, and (Miss) F. M. G. Micklethwait, *T.*, 1912, **101**, 2298; *ibid.*, 1913, **103**, 2074; J. C. Cain and (Miss) F. M. G. Micklethwait, *ibid.*, 1914, **105**, 1437, 1442.

[49] J. Kenner and W. V. Stubbings, *ibid.*, 1921, **119**, 593.

[50] *Annalen*, 1880, **203**, 95.

as one of the products of the nitration of diphenic acid as also by the oxidation of the mixture of dinitrophenanthraquinones. It yields a diamino-acid on reduction, and may be converted into 2 : 2′-dinitrodiphenyl or into carbazole. Further details of information in regard to this acid will be welcomed. The new isomeride, m. p. 263°, is obtained as an ester, in accordance with the scheme :—
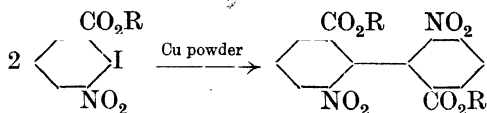
The behaviour of the acid on reduction is in sharp contrast with that of Schulze's substance, since a dilactam (XIII) is the sole product.

(XIII.)
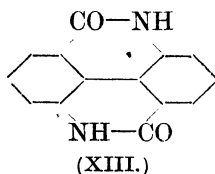
The suggestion is, therefore, that the substances are stereoisomerides of the annexed configurations :

Schulze's acid.   Kenner and Stubbings's acid.
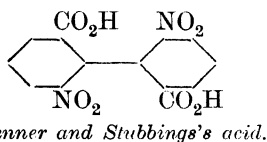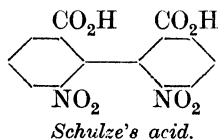
The assignment of these formulæ is made on the basis of the ring formation already referred to, but as an additional argument in favour of their correctness it should be noted that the particular methods of formation of the isomerides might be expected to lead to the observed results. The opening of the phenanthrene ring naturally leaves the carboxyl groups in something analogous to a *cis*-position, whilst the repulsion of similar groups accounts for the production of a substance possessing a *trans*-spatial character.

A fourth benzildioxime may be obtained by the addition of ammonium chloride to a solution of α-benzildioxime in aqueous sodium hydroxide which has been allowed to remain during two hours.[51] δ-Benzildioxime melts at 220° and is rapidly converted in alcoholic solution by acids or ammonia into the α-isomeride (m. p. 237°). It is characterised by the formation of a buff-coloured nickel compound, which passes with facility into the red nickel compound of α-benzildioxime and is thus differentiated from the

[51] F. W. Atack and L. Whinyates, *T.*, 1921, **119**, 1184.

similar nickel compound of γ-benzildioxime. The constitution of this interesting substance has not yet been fully elucidated, but its existence cannot be explained by the conventional Hantzsch-Werner hypothesis unless this be extended by the admission of the possible existence of structural isomerides. Atack considers [52] that the isomerism in the group of the oximes is more probably structural than geometrical and in a general discussion of the subject makes out a strong case in support of his thesis. It is not, however, yet possible to regard the problem as solved, although it is clear that the stereochemical theory in its simplest form is inadequate.

Natural Products.

A new monocyclic terpene has been found [53] in the oil of *Mosla japonica*, Maxim. Moslene nitrosochloride on treatment with sodium ethoxide yields among other products an azo-compound identical with that obtained by the reduction of 2-nitro-*p*-cymene. From this and other considerations it may be deduced that moslene must have the constitution (XIV) or (XV)
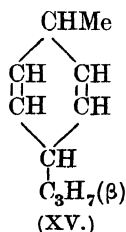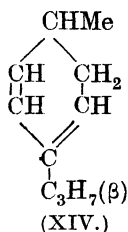
Later [54] the terpene was proved to exist in other essential oils containing *p*-cymene.

Piperitone, the peppermint ketone of eucalyptus oils, has been investigated and characterised by numerous derivatives. It has the formula $C_{10}H_{16}O$ [55] and may be oxidised to thymol by ferric chloride or catalytically reduced to menthone. Another paper [56] deals with its characteristic benzylidene and other derivatives and contains a brief account of the relation of the occurrence of piperitone to the botanical characters of the genus *Eucalyptus* and to the other oil constituents.

The oil from the grass *Andropogon Jwarancusa*, Jones, contains a ketone, $C_{10}H_{16}O$, to the extent of about 80 per cent. of the whole,

[52] *T.*, 1921, **119**, 1175.
[53] Y. Murayama, *J. Pharm. Soc. Japan*, 1921, 769; *A.*, i, 875.
[54] *Idem, ibid.*, No. **475**, 786; *A.*, i, 875.
[55] Smith and Penfold, *J. Proc. Roy. Soc. N.S. Wales*, 1920, **54**, 40.
[56] J. Read and H. G. Smith, *T.*, 1921, **119**, 779.

the identity of which with d-piperitone [57] is considered to be beyond doubt.[58]   A conclusive proof is afforded that this grass-oil ketone is d-Δ^1-p-menthen-3-one (XVI) and its benzylidene derivative is represented by the formula (XVII)

$$
\begin{array}{cc}
\text{Me} & \text{Me} \\
\mid & \mid \\
\text{C} & \text{C} \\
\diagup\ \diagdown & \diagup\ \diagdown \\
\text{CH}_2\quad\text{CH} & \text{PhCH:C}\quad\text{CH} \\
\mid\qquad\mid & \mid\qquad\mid \\
\text{CH}_2\quad\text{CO} & \text{CH}_2\quad\text{CO} \\
\diagdown\ \diagup & \diagdown\ \diagup \\
\text{CH} & \text{CH} \\
\mid & \mid \\
\text{C}_3\text{H}_7(\beta) & \text{C}_3\text{H}_7 \\
\text{(XVI.)} & \text{(XVII.)}
\end{array}
$$
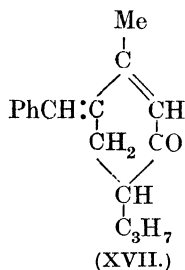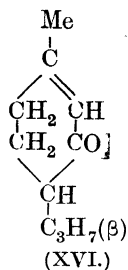
There is of course no difficulty in accepting the latter suggestion in view of the well-known fact that unsaturated atoms are efficient transmitters of the activating influence of a carboxyl group.   The constitution (XVI) has also been assigned to piperitone from eucalyptus oil in view of the observation that this substance may be oxidised to 2-hydroxy-Δ^1-menthen-3-one.[59]

Pikamar, a constituent of beechwood tar, has been synthesised [60] by an application of the Claisen transformation and thus shown to be 4-hydroxy-3 : 5-dimethoxy-n-propylbenzene.   The synthesis is illustrated in the annexed scheme :—

$$
\underset{\text{MeO}}{\text{CH}_2\text{:CH·CH}_2\text{·O}}\!\!\bigcirc \;\longrightarrow\; \underset{\text{MeO}}{\text{HO}}\bigcirc\text{CH}_2\text{·CH:CH}_2 \quad \xrightarrow[\text{hydrolysis}]{\text{acetylation, catalytic reduction,}}
$$

$$
\underset{\text{MeO}}{\overset{\text{HO}}{}}\bigcirc\text{CH}_2\text{·CH}_2\text{·CH}_3
$$
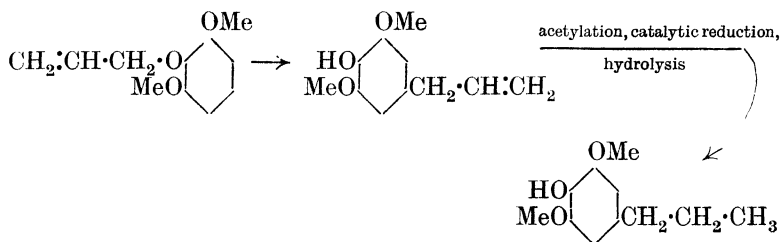
A crystalline constituent of Siamese benzoin termed lubanyl benzoate is apparently the benzoate of coniferyl alcohol having the constitution

$$
\text{HO}\underset{}{\overset{\text{OMe}}{\bigcirc}}\text{CH:CH·CH}_2\text{·OBz,}
$$
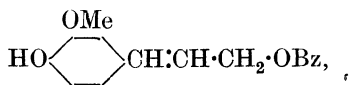
[57] Piperitone occurs, however, in an inactive form in eucalyptus oils.

[58] J. L. Simonsen, *T.*, 1921, **119**, 1644.

[59] L. Givaudan & Co., *Perf. Essent. Oil Rec.*, 1921, **12**, 80; *A.*, i, 793.

[60] F. Mauthner, *J. pr. Chem.*, 1921, [ii], **102**, 36; *A.*, i, 726.

but the actual isolation of the alcohol has hitherto proved impossible on account of its instability to alkali and acid.[61]

The liquors from the sulphite-cellulose process contain a crystalline lactone, $C_{20}H_{20}O_6$, which may be obtained by extraction with ether. The constitution XVIII or XIX is suggested for this substance as the result of a study of its transformations,[62]

(XVIII.) (XIX.)
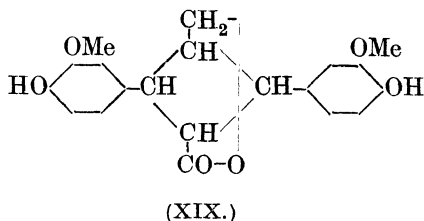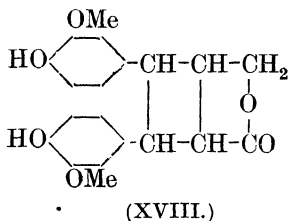
and of these, XVIII is probably to be preferred in view of the proved structure of guaiaretic acid. The substance is of interest as constituting another member of the growing class of di-eugenol derivatives.

The resin acids have been the subject of several communications, of which a theoretical paper on the constitution of abietic acid may be mentioned as containing some important suggestions.[63] The formula evolved for abietic acid is
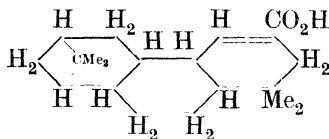
and this is derived from the condensation of a molecule of α-pinene with one of β-pinene followed by oxidation of a methyl group to carboxyl. This is a line of argument which is sure to be fundamentally sound, but the particular interpretation does not square very well with the results of other work which now falls to be discussed. O. Aschan [64] has isolated and carefully characterised a new crystalline resin acid, pinabietic acid, $C_{20}H_{30}O_2$, from the less volatile fractions obtained on distilling pine oil in a current of superheated steam. The constitutional investigation conducted by

[61] A. Zinke and J. Dzrimal, *Monatsh.*, 1920, **41**, 423; *A.*, i, 187; F. Reinitzer, *Arch. Pharm.*, 1921, **259**, 60; *A.*, i, 352.

[62] B. Holmberg, *Svensk Kem. Tidskrift*, 1920, **32**, 56; *A.*, i, 25; *Ber.*, 1921, **54**, [B], 2389; *A.*, i, 849; B. Holmberg and M. Sjöberg, *ibid.*, 2406; *A.*, i, 850.

[63] Ad. Grün, *Zeit. Deut. Ol. Felt-ind.*, 1921, **41**, 49; *A.*, i, 344.

[64] *Annalen*, 1921, **424**, 117; *A.*, i, 669.

A. I. Virtanen [65] has given the following results. Pinabietic acid contains one double bond (saturated dibromide and dihydro-derivative) and one bridged ring (dihydrobromide).

In spite of the fact that the acid can be nitrated and sulphonated, the presence of an aromatic nucleus is improbable on account of the empirical composition, the behaviour towards the reagents for the double bond, and also in view of the values obtained for the refractive powers of the esters. The latter are difficult to prepare, and also to hydrolyse when once formed.

Pinabietyl chloride evolves carbon monoxide and hydrogen when distilled under reduced pressure and furnishes a hydrocarbon, $C_{19}H_{28}$, called pinabietene. The latter contains an aromatic nucleus and is octahydromethylretene, since it may be changed to retene by heating with sulphur, the reaction involving the loss of hydrogen and a methyl group. Further, the oxidation of pinabietene by nitric acid or by manganese dioxide and sulphuric acid produces benzene-1 : 2 : 4-tricarboxylic acid. The formulæ suggested for pinabietene and pinabietic acid are XX and XXI respectively, although it is admitted that the positions of the double bonds, cross-linking and methyl group marked with an asterisk, are still doubtful.

(XX.)   (XXI.)
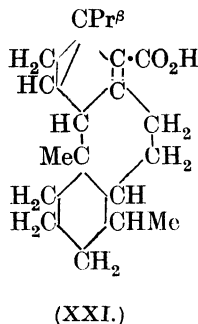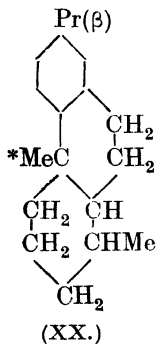
But the arguments cited are not at all conclusive, and that some modifications may be expected is clear from the fact that the above structures cannot be subdivided into units containing the arrangement of carbon atoms present in isoprene. This is possible in the case of all known substances of proved constitution which have a relation to the terpene series.

The synthesis of sinapic acid [66] has been effected through the stages :—

[65] *Annalen*, 1921, **424**, 150; *A.*, i, 669.
[66] E. Späth, *Monatsh.*, 1920, **41**, 271; *A.*, i, 28.
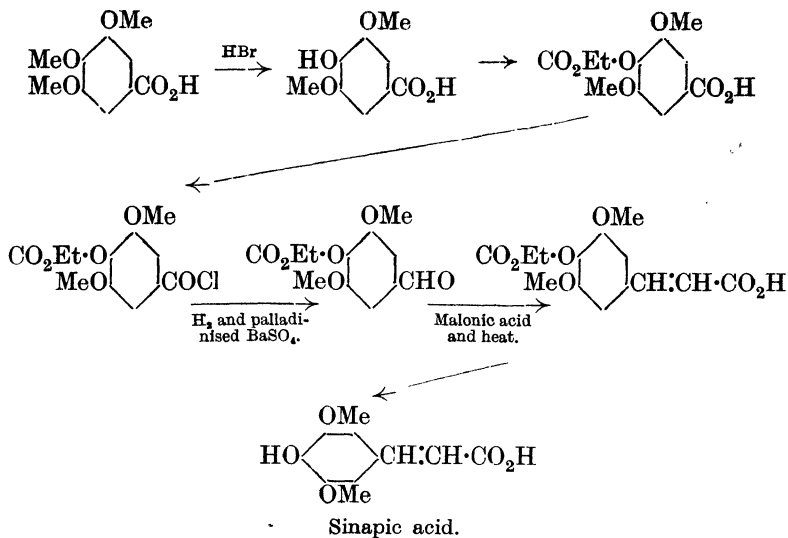
Sinapic acid.

Sinapic acid was then converted into sinapin iodide, identical with the salt of natural sinapin, by condensing acetylsinapoyl chloride with dimethylaminoethanol to β-dimethylaminoethyl acetylsinapate, which by gentle hydrolysis yielded the corresponding sinapate. The addition of methyl iodide now furnished sinapin iodide, $NMe_3I\cdot CH_2\cdot CH_2\cdot O\cdot CO\cdot CH\colon CH\cdot C_6H_2(OMe)_2\cdot OH$, thus confirming Gadamer's formula for sinapin.

Alicyclic Group.

It is quite impossible owing to limitations of space adequately to summarise the work of Thorpe, Ingold, Kon, and others on the related topics of the conditions governing the ease of formation and the stability of cyclic systems, and indeed a consideration of this group of papers emphasises the desirability of the system of publication from time to time of résumés by the original workers themselves of the position arrived at in the study of their problems. The theory that an alteration in the angle subtended by two of the valencies of a carbon atom involves a corresponding alteration in that enclosed by the remaining two has been again experimentally verified.[67] It is suggested that " if 2β be the angle formed by the valencies a and b, the angle 2θ between the directions taken up by the valencies c and d will be determined by the condition that these directions are equally inclined to each other and to the directions

[67] O. Becker and J. F. Thorpe, *T.*, 1920, **117**, 1579.

occupied by the valencies a and b." If 2β is known, it is shown that 2θ can be calculated by means of the equation

$$\text{Cos } \theta = \tfrac{1}{4}(\sqrt{\overline{\cos^2 \beta + 8}} \ \ - \cos \beta).$$

It must be pointed out that the experimental results support the sense of this assumption, but are not as yet capable of being brought into any quantitative relation with it.   In the series

$$
\begin{array}{ccc}
\underset{\text{Me}}{\text{Me}}\!\!>\!\!C\!<\!\!\begin{array}{c}\text{CH·CO}_2\text{H} \\ | \\ \text{CH·CO}_2\text{H}\end{array}, &
\begin{array}{c}\text{CH}_2\!\!-\!\!\text{CH}_2 \\ | \qquad\quad | \\ \text{CH}_2\!\!-\!\!\text{CH}_2\end{array}\!\!>\!\!C\!<\!\!\begin{array}{c}\text{CH·CO}_2\text{H} \\ | \\ \text{CH·CO}_2\text{H}\end{array}:
\end{array}
$$

Caronic acid.   (XXII.)

$$
\text{CH}_2\!<\!\!\begin{array}{c}\text{CH}_2\!\!-\!\!\text{CH}_2 \\ | \qquad\quad | \\ \text{CH}_2\!\!-\!\!\text{CH}_2\end{array}\!\!>\!\!C\!<\!\!\begin{array}{c}_{(d)}\text{CH·CO}_2\text{H} \\ | \\ _{(c)}\text{CH·CO}_2\text{H}\end{array},
$$

(XXIII.)
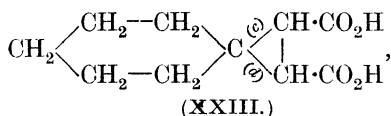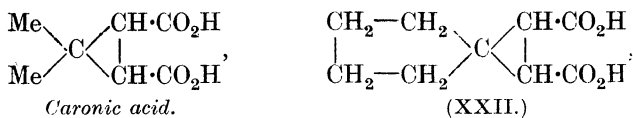
a and b are taken to be the valencies represented at the left of the quaternary carbon atom, and we may examine the effect of alterations in the angle between a and b by study of the stability of the *cyclo*propane ring.   It has already been shown [68] that in the case of the *cyclo*hexane derivative XXIII the *cyclo*propane ring is unusually stable and resists the action of concentrated hydrochloric acid at 240°, whereas caronic acid is attacked readily and even at 200° by 5 per cent. acid.   Here the enlargement of the normal angle between a and b renders the angle between the valencies c and d in (XXIII) smaller without strain and consequently the *cyclo*propane ring is more stable.   Now the angle in a symmetrical *cyclo*pentane ring differs from the normal angle between unstrained carbon valencies by about 18′ only, and the substance (XXII) should therefore from the present point of view closely resemble caronic acid in respect of the stability of its *cyclo*propane ring.   This was found to be the case, and the distinction in properties between XXII and XXIII is unexceptionable evidence in favour of the fundamental theory. Other comparisons were instituted with similar results.

Progress has been made [69] in the attempt to synthesise *spiro*-hydrocarbons which on account of their simplicity may be expected to furnish valuable evidence relating to the nature of valency as it occurs in carbon compounds.

Up to the present, the dihydroresorcinol derivatives (XXIV) and (XXV) have been prepared by the addition of ethyl sodiomalonate to the unsaturated ketones (XXVI) and (XXVII) followed by hydrolysis of the products.   The success of this process

[68] C. K. Ingold and J. F. Thorpe, *T.*, 1919, **115**, 320.
[69] W. S. G. P. Norris and J. F. Thorpe, *ibid.*, 1921, **119**, 1199.

proves that the condensation product of *cyclo*hexanone and acetone has the constitution figured (XXVI), and not that (XXVIII) ascribed to it by Wallach on the ground of optical properties. The substance is a true analogue of mesityl oxide, and it is remarkable that it does not exhibit the usual exaltation of refractive power associated with endocyclic compounds and with $\alpha\beta$-unsaturated ketones.

$$CH_2 \Big\langle {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} {>} C {<} {}^{CH_2 \cdot CO}_{CH_2 \cdot CO} {>} CH_2 \qquad {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} {>} C {<} {}^{CH_2 \cdot CO}_{CH_2 \cdot CO} {>} CH_2$$

(XXIV.)   (XXV.)

$$CH_2 {<} {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} {>} C{:}CH \cdot COMe \qquad {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} {>} C{:}CH \cdot COMe$$

(XXVI.)   (XXVII.)

$$CH_2 {<} {}^{CH_2 \cdot CH_2}_{CH_2 - CH} {\gg} C \cdot CH_2 \cdot COMe$$

(XXVIII.)
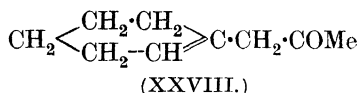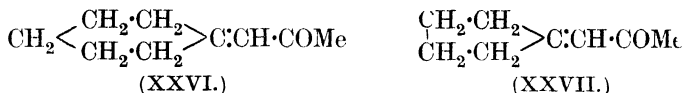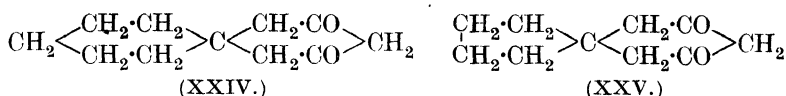
Another incidental result of the work under discussion is the disposal of Vorländer's somewhat bizarre conception that the dibromo-derivative of dimethyldihydroresorcinol should be formulated as a bromoxy-compound (XXIX). The bromination and subsequent chlorination and vice versa of dimethyldihydroresorcinol yield one and the same substance, which has accordingly the constitution (XXX).

$$Me_2C {<} {}^{CH_2 \cdot CO}_{CH_2 - C} {>} CBr \qquad Me_2C {<} {}^{CH_2 \cdot CO}_{CH_2 \cdot CO} {>} CBrCl$$
$$\qquad\qquad OBr$$

(XXIX.)   (XXX.)
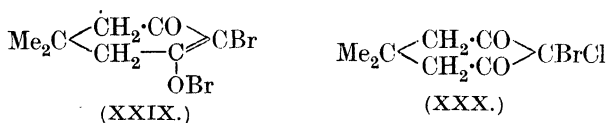
The ready elimination by means of alkali of one halogen atom from these and similar substances in the form of a hypobromite is referred to the general tendency to acquire a hydrogen atom necessary for tautomerism. The pronounced electropositivity of bromine in α-bromo-ketones is, however, a very general phenomenon, and is exhibited in cases such as ethyl bromoacetoacetate where the possibility of tautomerism already exists. The polar character of the bromine follows from the principle of induced latent polarity of atoms, but even so the gap in reactivity existing between the first and second bromine atoms certainly requires explanation.

Ingold (see below) has pointed out that the *gem*-dialkyl group has a remarkable effect in promoting the formation of cyclic structures, and it is found on calculation that the $\beta\beta$-dialkylglutaric acids occupy intermediate positions between glutaric and adipic acids in respect of the stability of cyclic ketones into which they

might be converted by distillation of their calcium salts. Actually it was found that the *cyclo*butanones were formed, but at the high temperature of the reaction underwent isomerisation. Thus ββ-dimethylglutaric acid yielded mesityl oxide.

$$Me_2C{<}{CH_2 \cdot CO \cdot O \atop CH_2 \cdot CO \cdot O}{>}Ca \rightarrow Me_2C{<}{CH_2 \atop CH_2}{>}CO \rightarrow Me_2C{:}CH \cdot COMe.$$
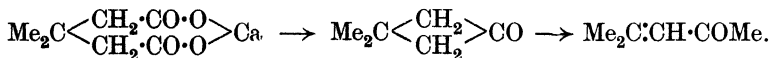
Other *gem*-dialkylglutaric acids behaved similarly, but no trace of unsaturated ketone could be obtained from the calcium salts of glutaric acid and of β-methylglutaric acid.[70]

C. K. Ingold has published a series of important researches on the subject of the conditions underlying the formation of unsaturated and cyclic compounds, which he prefaces in the first paper [71] by an account of a new and very interesting hypothesis relating to the calculation of the angles between carbon-to-carbon valencies. He suggests that the atoms joined to a carbon atom may be considered to occupy spherical domains, the cubic contents of which are proportional to the atomic volume of the element. These spheres are presumed to be in mutual contact and also with an internal sphere, and if now the centres of two of the external spheres are joined, the angle between the valencies is that subtended by this line at the centre of the internal sphere. These angles are readily calculated, and in a polymethylene chain the angle between carbon-to-carbon valencies is nearly 6° greater than has hitherto been supposed.

A very interesting result which follows is that the ease of formation of polymethylenes should be in the order *cyclo*hexane>*cyclo*pentane>*cyclo*propane>*cyclo*butane>*cyclo*heptane. This is in excellent agreement with thermochemical data and general chemical experience, especially the difficulty of producing *cyclo*butane derivatives. The powerful ring-promoting properties of the *gem*-dialkyl grouping is easily accounted for on these lines, although it still remains a mystery why the *cyclo*butanedicarboxylic acid (XXXI) should be so easily obtained, and many attempts to synthesise norpinic acid (XXXII) have always failed.

$$CO_2H \cdot CH{<}{CH_2 \atop CH_2}{>}CH \cdot CO_2H \qquad CO_2H \cdot CH{<}{CMe_2 \atop CH_2}{>}CH \cdot CO_2H$$
(XXXI.) (XXXII.)
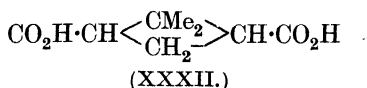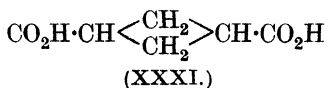
Some striking instances of the effect are recalled; the fact that all known β-lactones contain the *gem*-dimethyl grouping, the stability of ββ-dimethylglutaric anhydride, and the observation of Perkin and Thorpe that αββ-trimethylglutaric anhydride crystallises from water with solvent of crystallisation.

In adopting a plan of campaign with the object of testing this

[70] G. A. R. Kon, *T.*, 1921, **119**, 810.   [71] *Ibid.*, 305.

theory of the effect of atomic volumes on valency-to-valency angles, it was thought desirable to study a reaction which proceeds partly to a cyclic substance and partly in other directions, and the action of alkali hydroxides on α-bromo-dibasic acids was chosen. The normal products are a cyclic compound, an unsaturated substance, and a hydroxy-derivative. A detailed study of the action of concentrated sodium hydroxide on α-bromoglutaric acid and αα'-dibromoglutaric acid, diethyl α-bromo-glutaconate,[72] α-bromoadipic acid, and αα'-dibromoadipic acid [73] has been carried out and considerable experimental difficulties overcome in the isolation of a large proportion of the total product. The results are in general agreement with the theory, but do not lend themselves to summarisation in view of the large number of side reactions encountered.

Some compounds of novel type were prepared in the course of the work. Among these may be mentioned *cyclo*propanoldicarboxylic acid (XXXIII), obtained by the action of aqueous sodium carbonate on dimethyl αα'-dibromoglutarate. The first product is the corresponding bromo-acid.

XXXIII yielded *cyclo*propanone (XXXIV) by the action of concentrated sulphuric acid. The ketone was characterised by its semicarbazone.

$$CH_2 \Big\langle \begin{array}{c} C(OH) \cdot CO_2H \\ CH \cdot CO_2H \end{array} \qquad\qquad CH_2 \Big\langle \begin{array}{c} CO \\ CH_2 \end{array}$$

(XXXIII.)   (XXXIV.)
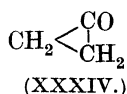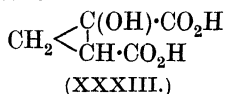
Ethyl bromoglutaconate was prepared by the action of diethylaniline on glutaconic ester dibromide, and this substance or αβ-dibromoglutaric acid, on treatment with alkali, gave rise among other substances to *cyclo*propenedicarboxylic acid (XXXV) and pyromellitic acid (XXXVI).

$$CH \Big\langle \begin{array}{c} CH \cdot CO_2H \\ C \cdot CO_2H \end{array} \quad or \quad CH_2 \Big\langle \begin{array}{c} C \cdot CO_2H \\ C \cdot CO_2H \end{array} \qquad \begin{array}{c} CO_2H \\ CO_2H \end{array} \Big\langle \bigcirc \Big\rangle \begin{array}{c} CO_2H \\ CO_2H \end{array}$$

(XXXV.)   (XXXVI.)
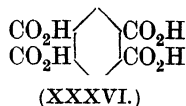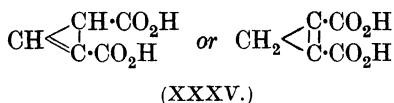
The stereoisomeric dibromo- and di-iodo-adipic esters, on boiling with 2N-sodium carbonate, gave good yields of muconic acid (XXXVII), which is thus for the first time an available substance, whilst a small yield of *cyclo*butene-1 : 2-dicarboxylic acid (XXXVIII) resulted under the same conditions from the so-called racemic esters only.

$$CO_2H \cdot CH \vdots CH \cdot CH \vdots CH \cdot CO_2H \qquad \begin{array}{c} CH_2 - C \cdot CO_2H \\ CH_2 - C \cdot CO_2H \end{array}$$

(XXXVII.)   (XXXVIII.)
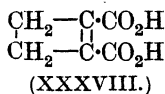
[72] E. H. Farmer and C. K. Ingold, *T.*, 1921, **119**, 2001.
[73] C. K. Ingold, *ibid.*, 951.

The configurations employed by Ingold for the dibromoadipic acids are different from those arrived at by the method already described (see above), but as they are deduced from the related tetrahydrofurandicarboxylic acids, the possibility of the occurrence of a Walden inversion must be taken into account. In order to harmonise the results, the Walden inversion would be required to occur in the case of the replacement of one bromine atom only, or, of course, there could be a double inversion in the one series and inversion at only one of the asymmetric carbon atoms in the other. In any case, the further investigation of the problem would be of much interest.

Pinene Derivatives.—Very considerable progress towards the goal of the complete synthesis of pinene has been recorded [74] and this most important of all terpenes can now be produced from pinonic acid (XXXIX).

Ethyl *r*-pinonate condenses with ethyl chloroacetate in presence of sodium ethoxide to a glycidic ester, from which the acid XL is obtained on hydrolysis. The latter substance is converted on heating at 230° in a vacuum to the semi-aldehyde of homopinocamphoric acid (XLI), readily oxidised to homopinocamphoric acid (XLII). Thence *r*-pinocamphone (XLIII) is obtainable by applying the Dieckmann reaction. α-Pinene (XLIV) has been already obtained by Tschugaeff [75] from the corresponding alcohol, pinocampheol, by the xanthogenate reaction and now from a pinocamphylamine by the method of exhaustive methylation.[76] The base employed in the latter process is a stereoisomeride of the known pinocamphylamine of Wallach and of Tilden, and is obtained by the hydrogenation of pinylamine, which latter is proved [77] to be a β-pinene derivative (XLV). It does not appear to have been actually prepared from pinocamphone.

$$CO_2H \cdot CH_2 \cdot CH < \!\!\! \begin{array}{c} CMe_2 \\ CH_2 \end{array} \!\!\! > CH \cdot COMe$$

(XXXIX.)

$$CO_2H \cdot CH_2 \cdot CH < \!\!\! \begin{array}{c} CMe_2 \\ CH_2 \end{array} \!\!\! > CH \cdot CMe < \!\!\! \begin{array}{c} CH \cdot CO_2H \\ O \end{array}$$

(XL.)

$$CO_2H \cdot CH_2 \cdot CH < \!\!\! \begin{array}{c} CMe_2 \\ CH_2 \end{array} \!\!\! > CH \cdot CHMe \cdot CHO$$

(XLI.)
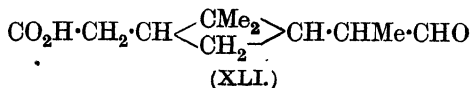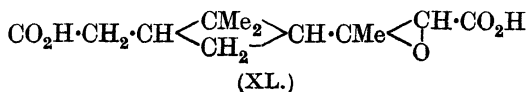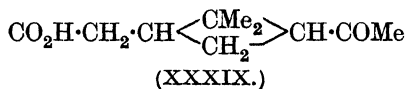
[74] L. Ruzicka and H. Trebler, *Helv. Chim. Acta*, 1921, **4**, 666; *A.*, i, 796.
[75] *A.*, 1908, i, 93.
[76] L. Ruzicka and H. Trebler, *Helv. Chim. Acta*, 1920, **3**, 756; *A.*, i, 36.
[77] *Ibid.*, 1921, **4**, 566; *A.*, i, 573.

$$\overset{}{..}_2\text{H}\ \ \overset{}{..}_2\ \ \overset{}{..}\diagdown\text{CH}_2\diagup\overset{}{..}\ \ \overset{}{..}\ \ \overset{}{..}_2\text{H}$$

(XLII.)

$$\begin{array}{ccc}
\text{CO} & \text{CH} & \overset{\displaystyle \overset{NH_2}{|}}{CH} \\
\diagup\ \diagdown & \diagdown\!\!\diagdown\ \diagdown & \diagup\ \diagdown \\
\text{MeCH}\quad\text{CH}_2 & \text{MeC}\quad\text{CH}_2 & \text{CH}_2\!:\!\text{C}\quad\text{CH}_2 \\
|\ _{CH_2}| & |\ _{CH_2}| & |\ _{CH_2}| \\
\text{CH}\quad\text{CH} & \text{CH}\quad\text{CH} & \text{CH}\quad\text{CH} \\
\diagdown\ \diagup & \diagdown\ \diagup & \diagdown\ \diagup \\
\text{CMe}_2 & \text{CMe}_2 & \text{CMe}_2 \\
\text{(XLIII.)} & \text{(XLIV.)} & \text{(XLV.)}
\end{array}$$
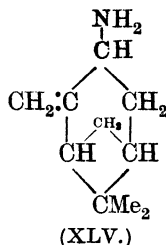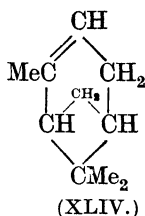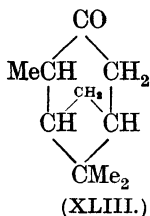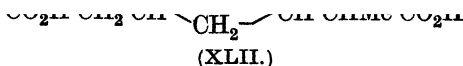
It has been demonstrated [78] that the action of dry hydrogen chloride on pinene at low temperatures does not yield bornyl chloride, but a true pinene hydrochloride, which is a liquid. This *tert.*-pinene hydrochloride is only stable below $-10°$, and in the absence of cooling changes spontaneously to solid bornyl chloride with evolution of heat.

Polynuclear Types.

Hydrindene Group.—Hydrindene itself has not previously been closely studied. It can be easily obtained in quantity by the hydrogenation of crude indene,[79] and its behaviour resembles that of tetrahydronaphthalene. A very large number of diketohydrindenes have been prepared by condensing aromatic hydrocarbons with dimethyl- and diethyl-malonyl chlorides with the aid of aluminium chloride.[80] The observation that diethylmalonyl chloride is far more suitable than the dimethyl compound for the preparation of alkylated diketohydrindene derivatives from phenolic ethers is perhaps an example of the application of Ingold's hypothesis which is discussed above.

Naphthalene Group.—Hydrogenated naphthalene derivatives have engrossed much attention recently, partly, no doubt, because tetrahydronaphthalene is now an article of commerce. The important discovery made by Rowe and referred to last year, that the reduction of naphthalene by means of sodium and alcohol leads to Δ^2-dihydronaphthalene, which is only hydrogenated further after isomerisation to the Δ^1-isomeride, has been found to have its parallel in the cases of the reduction of α-naphthylamine and

[78] O. Aschan, *Öfvers. Finska Vet.-Soc.*, 1914, 57, [A], No. 1, 35 pp.; A., 1921, i, 795.

[79] W. Borsche and M. Pommer, *Ber.*, 1921, 54, [B], 102; A., i, 168.

[80] K. Fleischer, *Annalen*, 1921, 422, 231; A., i, 251; K. Fleischer and F. Seifert, *ibid.*, 272; A., i, 254.

α-naphthol.[81] In each case a 5 : 8-dihydro-derivative is first formed and subsequently isomerised by the action of a sodium alkyloxide solution at a suitable concentration and temperature. It is not known whether the Δ^1-derivatives produced in this series of experiments are 5 : 6- or 7 : 8-dihydro-compounds (XLVI and XLVII),

NH₂ (or OH)   CH₂ NH₂ (or OH)

CH₂   CH₂

CH₂
(XLVI.)   (XLVII.)
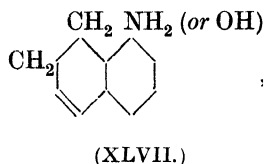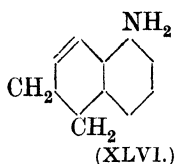
but apparently only one of these is obtained. Theoretical considerations indicate the second alternative as most probably the correct representation of the constitution of these substances.

The work of Rowe on the reduction of naphthalene has been confirmed by F. Straus and L. Lemmel, who have made a very thorough study of the transformations of Δ^1-dihydronaphthalene [82] so as to compare the behaviour of the substance with that of propenylbenzene. The dibromide of the hydrocarbon yields 2-bromo-1-hydroxynaphthalene (XLVIII) by the action of magnesium carbonate in aqueous acetone. This substance may be oxidised to a bromo-ketone yielding 1-keto-tetrahydronaphthalene (XLIX) on reduction. On the other hand, the bromohydrin (XLVIII) is converted by alcoholic potassium hydroxide to an ethylene oxide (L), which is transformed into 2-keto-tetrahydronaphthalene (LI) by treatment with dry hydrogen chloride.

CH·OH   CO

CHBr   CH₂

CH₂   CH₂

CH₂   CH₂
(XLVIII.)   (XLIX.)

O   CH₂

CH   CO

CH   CH₂

CH₂   CH₂

CH₂   CH₂
(L.)   (LI.)
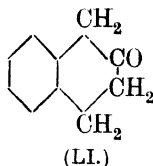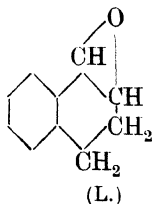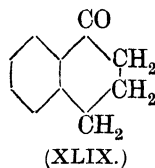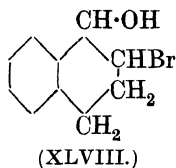
Δ^1-Dihydronaphthalene dibromide may be conveniently obtained

[81] F. M. Rowe and (Miss) E. Levin, T., 1920, 117, 1574; 1921, 119, 2021.

[82] F. Straus and L. Lemmel, Ber., 1921, 54, [B], 25; A., i, 170; F. Straus and A. Rohrbecker (and, in part, L. Lemmel), ibid., 40; A., i, 171.

by the bromination of tetrahydronaphthalene,[83] and the dihydro-naphthalene readily obtained by the action of zinc and alcohol on the dibromide. If, however, the alcohol is replaced by a non-hydroxylic solvent, an energetic reaction leads to the production of several compounds; among them the polymeride, $(C_{10}H_{10})_8$, a yellow powder. The action of sulphuric acid on a solution of the dihydronaphthalene in a hydrocarbon results in dimerisation to a crystalline product, m. p. 93°, together with oily isomerides.

A very ingenious attempt [84] to provide a synthetic substitute for the higher fatty acids depends on the catalytic reduction of α-naphthoyl-o-benzoic acid, $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot CO_2H$. This compound is potentially sufficiently cheaply prepared to meet the end in view, since it requires only naphthalene as the organic starting point. The acid is reduced by hydrogen in presence of oxygenated platinum to four stereoisomeric perhydro-α-naphthylmethylbenzoic acids, $C_{10}H_{17} \cdot CH_2 \cdot C_6H_{10} \cdot CO_2H$, a dihydro-acid containing the carbonyl group representing an isolable intermediate stage. The perhydro-acids have the constitution of stearic acid less six hydrogen atoms from positions 1, 6, 8, 12, 17, 17 due to the three rings contained, and their alkali salts are soaps corresponding approximately with those derived from fatty acids containing ten carbon atoms. The alkaline earth and heavy metal salts are soluble in hydrocarbons. In this connexion it may be mentioned that in the course of an extensive research which may ultimately indicate an entirely new method of constitutional analysis, W. B. Hardy has shown that no cyclic compound is an efficient lubricant of a bismuth to bismuth surface.[85]

Gattermann's synthesis of hydroxyaldehydes from phenols and hydrogen cyanide in presence of hydrogen chloride and zinc chloride, followed by hydrolysis of the aldimine hydrochloride, has been applied to the ten dihydroxynaphthalenes,[86] all of which undergo the synthesis, with production of thirteen (possibly more) dihydroxynaphthaldehydes, only one of which had previously been accurately described. The introduction of the substituent was found to proceed according to established rules, 2-naphthols being reactive in the 1-position and 1-naphthols in the 4-position and to a smaller extent in the 2-position. Curiously enough, 1 : 5-dihydroxynaphthalene gives the p-hydroxyaldehyde only, whilst 1 : 8-dihydroxynaphthalene gives rise to both o- and p-derivatives, the latter in very much greater relative amount. The oxidation of 1 : 7-dihydroxynaphthalene by means of lead peroxide in benzene

[83] J. von Braun and G. Kirschbaum, *Ber.*, 1921, **54**, [B], 597; *A.*, i, 407.

[84] R. Willstätter, D.R.-P. 325714; *A.*, i, 177; R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1921, **54**, [B], 1420; *A.*, i, 667.

[85] *Phil. Mag.*, 1920, [vi], **40**, 201; *A.*, 1920, ii, 534.

[86] G. T. Morgan and D. C. Vining, *T.*, 1921, **119**, 177.

suspension produces mainly a carbonate and a small yield of a dinaphtha-1 : 7-1' : 7'-diquinone, probably of the annexed constitution
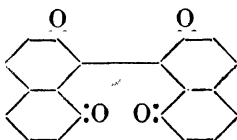
The diquinone forms a yellow, additive compound with benzene, $C_{20}H_{10}O_4,C_6H_6$, whilst the benzene-free compound crystallises in pale orange tablets which become bright red at 160°, reverting to the original colour on cooling.[87]　No adequate account is possible here of Morgan and Smith's researches on the constitution of simple and complex cobaltic lakes of various naphthaquinoneoximes,[88] but the subject must not be passed without an appreciative reference to a very successful application of the co-ordination theory. The paper is one which must be consulted in the original by all those who are interested in the problems of valency theory.

Acenaphthene Group.—β-Methoxyacenaphthenequinone (LII) is readily obtained by the condensation of β-naphthyl methyl ether and phenyloxaliminochloride with the help of aluminium chloride,[89] but this otherwise useful synthesis is not of general applicability.
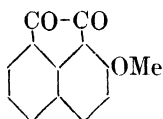
(LII.)
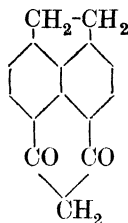
(LIII.)

Pericyclic derivatives of acenaphthene are not numerous, but may be obtained by the one-stage indanedione synthesis mentioned above. The most interesting example is that of the substance (LIII) prepared by the action of aluminium chloride on a mixture of malonyl bromide and acenaphthene in carbon disulphide solution.[90]

Anthracene Group.—As usual, there has been much activity evinced in the preparation of substituted anthraquinones, and the

[87] G. T. Morgan and D. C. Vining, *T.*, 1921, **119**, 1707.

[88] *Ibid.*, 704.

[89] H. Staudinger, H. Goldstein, and E. Schlenker, *Helv. Chim. Acta*, 1921, **4**, 342; *A.*, i, 433.

[90] K. Fleischer, H. Hittel, and P. Wolff, *Ber.*, 1920, **53**, [*B*], 1847; *A.*, 1920, i, 853.

results are on the whole in accord with previous experience and scarcely call for special attention. The various dibromoanthraquinones have been carefully oriented [91] and the conclusion has been reached that the dibromoanthraquinone employed by Graebe and Liebermann in the synthesis of alizarin must have been the 2 : 3- or 2 : 7-isomeride.

The products of the dinitration of anthraquinone are shown to be 1 : 5- (37 per cent.), 1 : 8- (37 per cent.), 1 : 7- (4·2 per cent.), 1 : 6- (3·6 per cent.), 2 : 6- (6 per cent.), 2 : 7- (4 per cent.), leaving only 8·2 per cent. unaccounted for and certainly due in part to losses in manipulation. The literature in this field contains the record of different results and the work under discussion will clear the air.[92]

Some novel results are recorded in a paper [93] which contains *inter alia* a description of a convenient process for the preparation of anthrone. Anthracene dibromide reacts with pyridine to form 9 : 10-dihydroanthraquinyldipyridinium dibromide (LIV), which yields anthrone (LV) in quantitative yield on boiling with water.

$$C_6H_4{<}^{CH(C_5H_5NBr)}_{CH(C_5H_5NBr)}{>}C_6H_4 \qquad\qquad C_6H_4{<}^{CH_2}_{CO}{>}C_6H_4$$

$$\text{(LIV.)} \qquad\qquad\qquad\qquad\qquad \text{(LV.)}$$

$$C_6H_4\underset{\text{(LVI.)}}{\overset{C_5H_5NBr}{\bigotimes}}C_6H_4 \qquad\qquad C_6H_4{<}^{CH(NRAr)}_{CH_2\text{———}}{>}C_6H_4$$
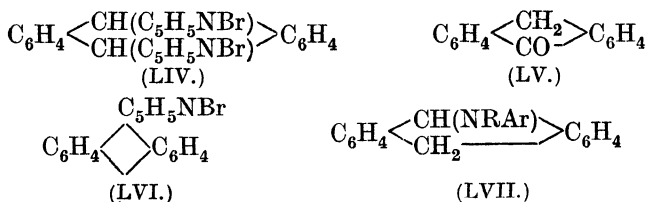
$$\text{(LVII.)}$$

The action of sodium hydroxide (or aliphatic amines) and of aromatic amines leads to the production of the stable anthranyl-pyridinium salt (LVI) and the reduced derivative (LVII) respectively. Scholl has proved [94] that the deep violet-blue compounds exhibiting striking fluorescences which Schaarschmidt [95] obtained by the reduction of 1-benzoylanthraquinones with aluminium or copper powder in concentrated sulphuric acid solution are actually a new class of compounds containing tervalent carbon. The product from 1-*p*-chlorobenzoylanthraquinone crystallises in violet-blue needles, m. p. 253°, and is represented as shown below. It is unimolecular in boiling nitrobenzene and has unsaturated properties, combining, for example, with *p*-benzoquinone just as triphenylmethyl does.

[91] M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632; *A.*, i, 349; Grandmougin, *Compt. rend.*, 1921, **173**, 717; *A.*, i, 871.

[92] M. Battegay and J. Claudin, *Bull. Soc. Ind. Mulhouse*, 1920, **86**, 628; *A.*, i, 350.

[93] E. de Barry Barnett and J. W. Cook, *T.*, 1921, **119**, 901.

[94] *Ber.*, 1921, **54**, [*B*], 2376; *A.*, i, 872.

[95] *A.*, 1915, i, 566, 696; 1916, i, 408.

$$\text{(structure: anthracene-like ring with O, HO, and } CO \cdot C_6H_4Cl)$$
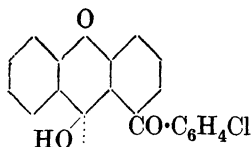
A reference may be made in this section to the surprising production of dihydrophenanthrene by the action of bromine on phenanthrene in glacial acetic acid solution in presence of sodium acetate.[96]

New Polynuclear Types.—The pyrogenic distillation of 1-phenylindene induces isomerisation to a new hydrocarbon not identical with 2-phenylindene.[97] The substance may be a *cyclo*butane derivative having either of the constitutions

$$C_6H_4{<}^{CH}_{CH}{>}CHPh \quad or \quad {}^{C_6H_4-CH}_{CH_2-CH}{>}C_6H_4$$
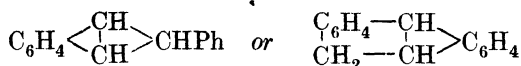
The main product of the thermal decomposition of acenaphthene is acenaphthylene (LVIII), but many other substances are formed [98] including colourless leucacene, which crystallises from benzene as the compound $4C_{54}H_{32},5C_6H_6$, violet rhodacene, bronze-red chalkacene, polyacenaphthylene, $C_{264}H_{176}$, and three chromacenes, one of which is black.

To chalkacene the formula (LIX) is assigned, and rhodacene is apparently regarded as a quinonoid form of the same arrangement of nuclei. Rhodacene is obtained by boiling leucacene with nitrobenzene, whereby acenaphthylene (2 mols.) is split off at the same time.

CH=CH

(LVIII.)   (LIX.)
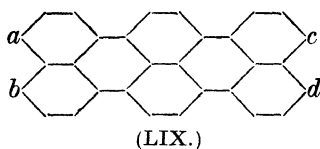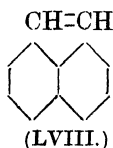
The formula of rhodacene contains four tervalent carbon atoms marked *a, b, c, d* in the chalkacene formula (LIX) and if this is really correct it is not surprising that isomerisation to chalkacene takes place under the influence of light or on continued boiling in nitrobenzene.

[96] F. Mayer and A. Sieglitz (with W. Ludwig), *ibid.*, [*B*], 1397; *A.*, i, 554.

[97] H. Henstock, *T.*, 1921, **119**, 1461.

[98] K. Dziewoński (with J. Podgórska, Z. Lemberger, and J. Suszka), *Ber.*, 1920, **53**, [*B*], 2173; *A.*, i, 105.

Compounds containing Silicon, Arsenic, and Metals.

The action of sodium oh diphenylsilicon dichloride is complex and results in the production of three crystalline compounds, two of which have been examined, as well as other substances.[99] The crystalline compounds both give values in molecular-weight determinations approximating to those required for the formula Si_4Ph_8. One of the substances is saturated, but the other readily forms an iodide, $Si_4Ph_8I_2$, and an oxide, Si_4Ph_8O. A second oxide, $Si_4Ph_8O_2$, is the result of the action of boiling nitrobenzene on the unsaturated silicohydrocarbon, whereas the isomeride crystallises unchanged from this solvent. No little difficulty is experienced in assigning formulæ to these substances, for the composition in each case suggests the constitution (LX). The iodide and oxide would then have the formulæ (LXI) and (LXII), whilst the dioxide is considered to be either (LXIII) or (LXIV). The isomerism of the " saturated " and " unsaturated " silicohydrocarbons may, it is thought, be explained on the basis that they are both octaphenyl-silicotetranes having silicon atoms in coplanar and tetrahedral arrangements respectively.

$$SiPh_2 \underset{SiPh_2}{\overset{SiPh_2}{<\hspace{1em}>}} SiPh_2$$
(LX.)

$$\begin{matrix} SiPh_2-SiPh_2I \\ | \quad\quad\quad | \\ SiPh_2-SiPh_2I \end{matrix}$$
(LXI.)

$$\begin{matrix} SiPh_2-SiPh_2 \\ | \quad\quad\quad | \quad >O \\ SiPh_2-SiPh_2 \end{matrix}$$
(LXII.)

$$\begin{matrix} SiPh_2-O-SiPh_2 \\ | \quad\quad\quad\quad | \\ SiPh_2-O-SiPh_2 \end{matrix}$$
(LXIII.)

$$SiPh_2 \underset{SiPh_2-O}{\overset{SiPh_2-O}{<\hspace{1em}>}} SiPh_2$$
(LXIV.)
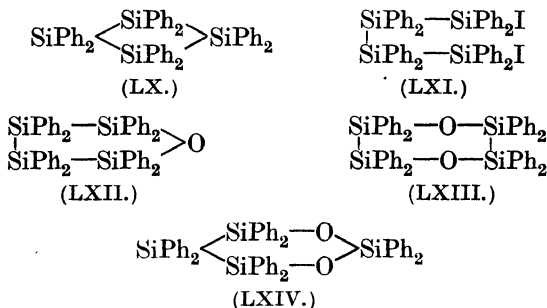
Much attention has been devoted to organic compounds of phosphorus, arsenic, antimony, and bismuth, but on account of limitations of space even some outstanding results cannot be discussed.

H. King [1] has tracked down the sulphur-containing constituent of salvarsan prepared by the hyposulphite reduction method and finds it to be 3 : 3′-diamino-4 : 4′-dihydroxy-5-sulphoarsenobenzene monohydrochloride,

$$HO \underset{}{\overset{NH_3Cl}{\bigcirc}} As_2 \underset{SO_3H}{\overset{NH_2}{\bigcirc}} OH$$
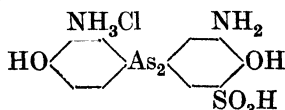
[99] F. S. Kipping and J. E. Sands, *T.*, 1921, **119**, 835.
[1] *Ibid.*, 1107, 1415.

The new o-aminophenolsulphonic acid which can be obtained by hydrolysis of this arsenobenzene derivative has been synthesised, and the mechanism of the introduction of the sulphonic group is an interesting problem.

The application of the diazo-synthesis to the production of aryl-arsinic [2] and aryl-stibinic [3] acids has been studied with valuable results, including the determination of the optimal conditions for the reaction; thus, for example, in the case of the arsinic acids the alkalinity of the solution should be regulated so that the process can occur in accordance with the equation :—

$$PhN_2Cl + AsO_3HK = AsPhO_3HK + KCl + N_2.$$
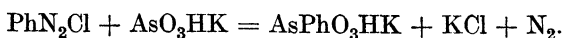
In the case of the stibinic acids, the solution may be alkaline, and a really convenient process for the production of aryl antimony derivatives is available. The aryl-stibinic acids are apparently derived from a polymerised antimonic acid, and are pronouncedly colloidal in their properties. Phenylstibine tetrachloride, $PhSbCl_4$, is obtained from phenylstibinic acid by the action of concentrated hydrochloric acid; on heating, it dissociates into chlorine and phenyldichlorostibine, $PhSbCl_2$, and the latter undergoes further decomposition with the production of diphenylchlorostibine, Ph_2SbCl, and antimony chloride. The action of sulphurous acid on phenylstibinic acid leads to phenylstibinic oxide, PhSbO, and more energetic reduction produces stibiobenzene, PhSb:SbPh, which is a brown, amorphous powder very susceptible to atmospheric oxidation.

A large number of arylbismuthine derivatives have been prepared [4] by applications of the Grignard reaction and from bismuth haloids and mercury diaryls. Thus bismuth bromide and mercury diphenyl interact with production of triphenylbismuthine in quantitative yield.

Triarylbismuthines react as a rule with bismuth haloids to produce diarylbismuthine haloids, but tri-α-naphthylbismuthine and bismuth bromide yield α-naphthylbismuthine dibromide in whatever proportion they are mixed.

The preparation of lead tricyclohexyl as a crystalline substance of molecular weight corresponding in dilute solution with the formula $Pb(C_6H_{11})_3$ places beyond doubt the existence of tervalent lead in organic compounds.[5] The substance is obtained by the addition of lead chloride to a solution of magnesium cyclohexyl bromide

[2] H. Schmidt, *Annalen*, 1920, **421**, 159; *A.*, 1920, i, 897.
[3] *Idem, ibid.*, 174; *A.*, 1920, i, 900.
[4] F. Challenger and C. F. Allpress, *T.*, 1921, **119**, 913.
[5] R. Krause, *Ber.*, 1921, **54**, [*B*], 2060; *A.*, i, 825.

in ether, and is readily converted by iodine into lead tri*cyclo*hexyl iodide. In view of its unsaturated character the compound is compared with triphenylmethyl.

I desire to thank Miss M. Jobson, M.A., B.Sc., for much assistance in drawing up the foregoing report. The period covered includes December 1920 and 1921.

R. ROBINSON.

PART III.—HETEROCYCLIC DIVISION.

ALTHOUGH the general level of interest of the work published this year is perhaps somewhat lower than that dealt with last year, a very small proportion is such that it can reasonably be passed unnoticed in an Annual Report. This fact, with a decided increase in the volume of work published, and the Reporter's desire to supply sufficient detail for a reasonable grasp of the topics reviewed in the limited space at his disposal, must explain any terseness of expression.

Ring Formation.

The synthetical operations recorded during the period under review afford a number of illustrations of the various influences which affect the process of ring formation; these it seems preferable to consider collectively rather than under the separate classes of compounds from which they are drawn.

The syntheses of the seven-membered rings contained in homomorpholine (I) and its benzo-derivative (II) are of the usual type, but require careful adherence to special conditions and furnish very moderate yields : [1]

$$PhN{<}^{[CH_2]_3 \cdot OH}_{[CH_2]_2 \cdot OH} \xrightarrow{70\% \ H_2SO_4} PhN{<}^{[CH_2]_3}_{[CH_2]_2}{>}O \longrightarrow$$

$$NO \cdot C_6H_4 \cdot N{<}^{[CH_2]_3}_{[CH_2]_2}{>}O \longrightarrow HN{<}^{[CH_2]_3}_{[CH_2]_2}{>}O$$

(I.)

(II.)
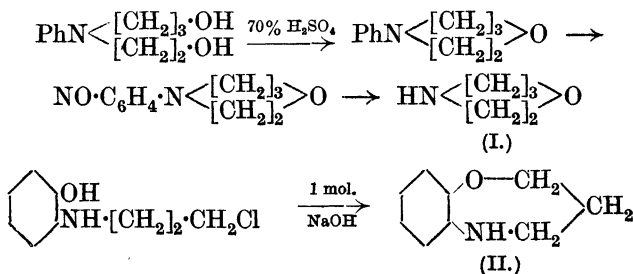
The products, however, which are strongly basic, when once obtained do not exhibit any particular instability.

[1] J. von Braun and O. Braunsdorf, *Ber.*, 1921, **54**, [*B*], 685; *A.*, i, 435.

E 2*

It would appear that the influences, familiarly grouped under the term "steric," have much less influence on intramolecular than on intermolecular reactions.[2]   Thus, by the action of aluminium chloride on the requisite oxalyl chlorides, of the type (III), the coumarandiones (IV—VIII) are readily obtained.[3]   The formation of 5-methylcoumarandione (IV) rather than its 3-methyl isomeride is not necessarily due to steric causes, since the alkyl group in such reactions is known to exert a para-directive influence.   The presence of the methyl group in the meta-position to the oxygen atom has an important influence on the result, comparable with

ArO·CO·COCl

(III.)   (IV.)   (V.)

(VI.)   (VII.)   (VIII.)
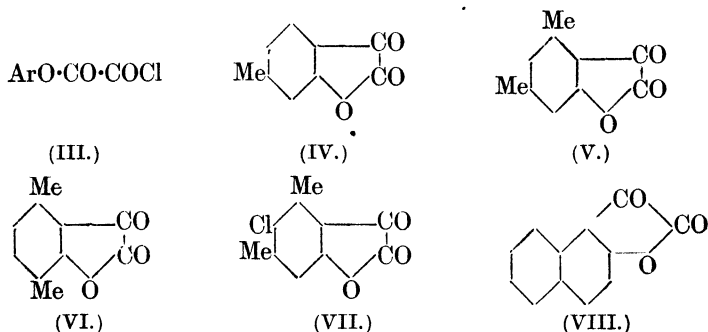
its favourable influence on the stability of coumaranones.[4]   Thus, from phenyloxalyl or p-tolyloxalyl chloride, in place of coumarandiones, o-hydroxybenzoyl chlorides and carbon monoxide are produced :

$$\left[\text{Me} \underset{O}{\overset{CO}{\diagup}} + HCl \right] \rightarrow \left[Me \underset{OH}{\overset{CO·COCl}{\diagup}} \right] \rightarrow$$

$$Me \underset{OH}{\overset{COCl}{\diagup}} + CO.$$
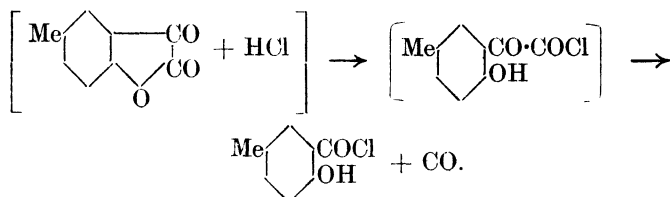
In connexion with this interesting reaction, it is worth noting that oxalyl chloride itself is decomposed by aluminium chloride into carbonyl chloride and carbon monoxide,[5] and that no signs of para-compounds could be detected among the products from phenyloxalyl chloride.   These facts, together with the well-known tendency of aluminium chloride to effect hydrolysis, suggest that the products in brackets may represent intermediate stages in the

[2] Compare J. Kenner and E. Witham, *T.*, 1921, **119**, 1452.
[3] R. Stollé and E. Knebel, *Ber.*, 1921, **54**, [*B*], 1213; *A.*, i, 578; H. Staudinger, E. Schlenker, and H. Goldstein, *Helv. Chim. Acta*, 1921, **4**, 434; *A.*, i, 432.
[4] K. von Auwers, *Annalen*, 1920, **421**, 1; *A.*, 1920, i, 866.
[5] H. Staudinger, E. Schlenker, and H. Goldstein, *loc. cit.*

reaction. Again, tetrahydrocarbazole is best prepared by an application of the well-known indole synthesis, consisting in boiling *cyclo*hexanonephenylhydrazone with glacial acetic acid, and this reaction has been successfully extended to the 2-chloro-5-nitro-phenylhydrazone (IX) : [6]
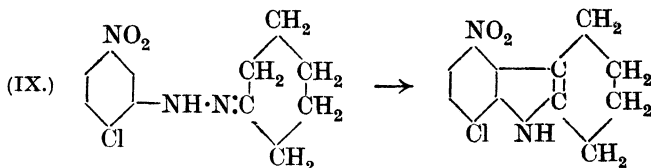
Another factor which appears to affect the formation of rings on two sides of a central benzene nucleus is some disinclination to their production in straight alignment, as typified by anthracene. The illustration, supplied in last year's Report,[7] of the formation of an acrylic acid rather than a coumarin, from 5-hydroxycou-marone-4-aldehyde by condensation with acetic anhydride and sodium acetate, has been confirmed.[8] Further, whereas ethyl 2 : 4-dinitro-5-hydrazinophenylacetate (X) is easily converted by alkali into an azimino-compound, according to the reaction usually exhibited by *o*-nitrophenylhydrazines,
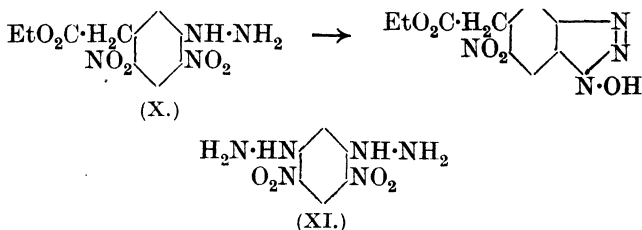
4 : 6-dinitro-1 : 3-dihydrazinobenzene (XI) is decomposed by alkali with evolution of gas.[9] That the resistance to the formation of a ring system of the anthracene type is not, however, always invincible, is shown by an investigation,[10] which has also cleared up the disputed question as to the mode of coupling of *m*-phenylenediamines. Thus, from benzeneazo-*m*-phenylenediamine (XII), a triazole derivative (XIII) is obtained by oxidation with ammoniacal copper

[6] W. H. Perkin, jun., and S. G. P. Plant, *T.*, 1921, **119**, 1825; compare Drechsel, *J. pr. Chem.*, 1888, [ii], **38**, 65; Baeyer, *Ber.*, 1889, **22**, 2185; *Annalen*, 1894, **278** 105; *A.*, 1888, 1276; 1889, 1162; 1894, 174.

[7] P. 102.

[8] P. Karrer, A. Rüdlinger, A. Glattfelder, and L. Waitz, *Helv. Chim. Acta*, 1921, **4**, 718; *A.*, i, 800.

[9] W. Borsche, *Ber.*, 1921, **54**, [B], 669.; *A.*, i, 461.

[10] M. P. Schmidt and A. Hagenböcker, *ibid.*, 2191; *A.*, i, 897; Kalle and Co., *Patentanmeldung*, K 60493, iv, 12 pp.

sulphate solution. Since only those substitution derivatives of this compound, as of β-naphthylamine, will couple further which have a free 4-position, benzeneazo-5-amino-2-phenyl-2 : 1 : 3-benz-triazole has the formula (XIV), and so furnishes a bistriazole of the constitution (XV). This product is also obtainable from the compound contained in the filtrate from the dye prepared by coupling *m*-phenylenediamine with two molecules of diazotised aniline. The dye itself may be converted into an isomeric compound, to which the formula (XVI) must be assigned :
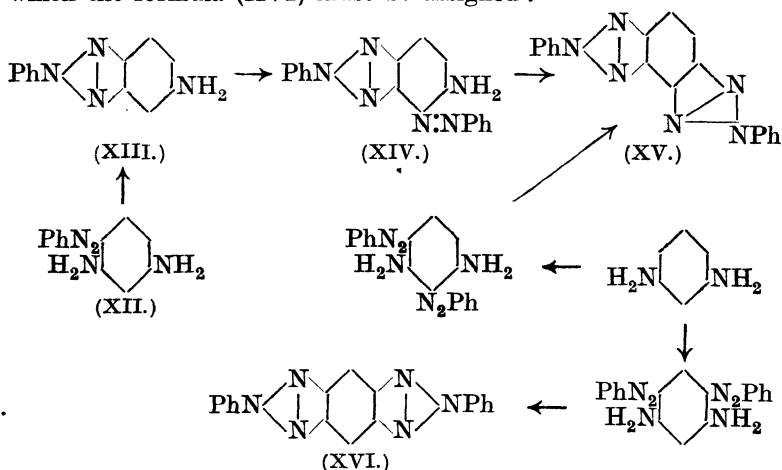
It therefore follows that coupling with *m*-phenylenediamine occurs in both the possible ways, a point in noteworthy contrast with the behaviour of the triazole derivative.

Further work has emphasised the intricacy of the conditions governing the formation of cyclic compounds from derivatives of *o*-hydroxyphenyl vinyl ketone.[11] Thus, it has long been known that the bromides of *o*-acetoxyphenyl styryl ketones (XVII) are converted by treatment with alkali in some cases into coumaranones (XVIII), in others into flavones (XIX), according to the nature and position of the substituents in the two nuclei :
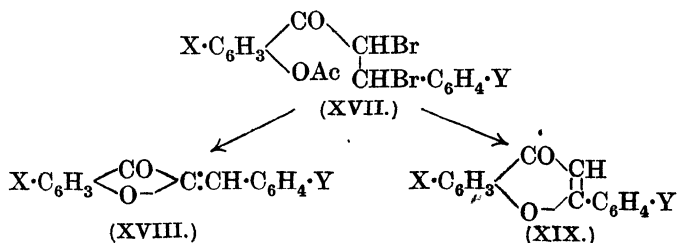
[11] Compare *Ann. Reports,* 1920, **17,** 101.

In explanation, it has been supposed that the former change occurs when the difficulty of hydrolysis permits the prior formation of the bromostyryl ketone, whilst the latter occurs when the acetyl group is easily hydrolysed.[12]   This is, however, not the case, since the dibromides of o-hydroxyphenyl styryl ketones may be converted into coumaranones by the addition of hot aqueous sodium hydroxide to their hot alcoholic solution, whilst at the ordinary temperature they yield flavones.   The result appears to be due to the simultaneous operation of two parallel reactions, the relative velocities of which are determined partly by external conditions, partly by the nature of the substituents in the benzene nuclei :
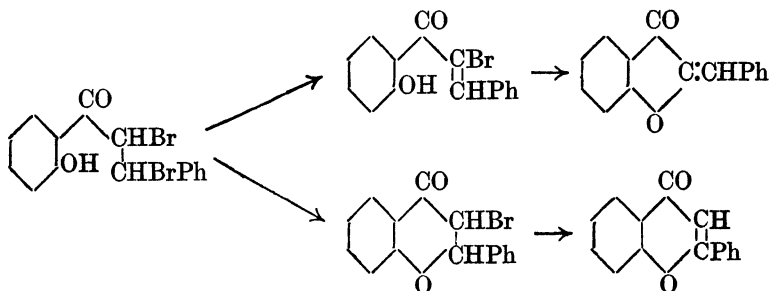
The especial instability of the five-membered ring in the 1-alkyl-coumaranones is apparently even more pronounced in the 1-phenyl derivatives.[13]   Thus, the action of sodium hydroxide on α-bromo-2-hydroxy-5-methyldeoxybenzoin (XX) should, according to the precedent of compounds containing an alkyl in place of a phenyl group in the side chain, give rise to 1-phenyl-4-methylcoumaranone (XXI).
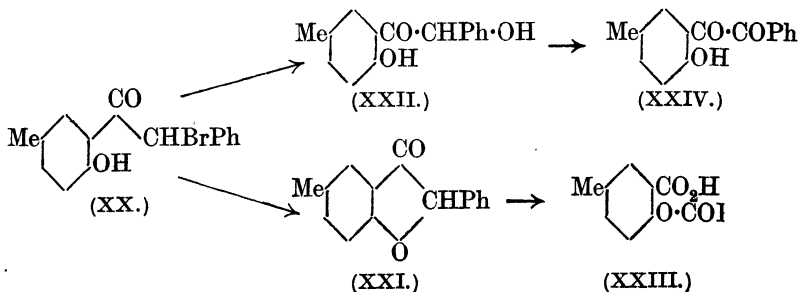
The product, however, after prolonged exposure to the atmosphere consists chiefly of 2-hydroxy-5-methylbenzil (XXIV), with a small

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[12] Kostanecki and Tambor, *Ber.*, 1899, **32**, 2268; *A.*, 1899, i, 891.

[13] K. von Auwers and L. Anschütz, *ibid.*, 1921, **54**, [*B*], 1543; *A.*, i, 682; compare *Ann. Reports*, 1920, **17**, 100.

amount of 4-benzoyloxy-*m*-toluic acid (XXIII), which result from oxidation of the intermediate deoxybenzoin (XXII) and coumaranone respectively.[14] It may be noted, however, that the methyl group probably contributes to the results, since the stability of coumaranones is diminished by the presence of such groups in the ortho- or para-position to the oxygen atom.

The results of the action of phenylhydrazine on the phenyl vinyl ketones are also interesting.[15] It is quite in accordance with anticipation that the formation of pyrazolines should become progressively more difficult as the ketone (XXV) is modified by the introduction of methyl groups in place of the hydrogen atoms of its methylene group :

$$PhCO \cdot CH{:}CH_2 \;\longrightarrow\; Ph\underset{\underset{N}{|}}{C} \cdot CH_2 \cdot \underset{\underset{NPh}{|}}{C}H_2$$
$$\text{(XXV.)}$$
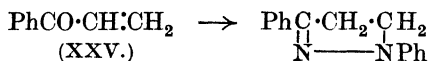
It may also be argued that the formation of a hydrazino-hydrazone (XXVI), with an azo-compound derived from it by oxidation, from 4-hydroxy-*m*-tolyl *iso*butenyl ketone [16] is due to the effect of the ortho-hydroxyl group in so diminishing the rate of hydrazone formation that addition occurs at the double bond with a relatively much greater velocity. Indeed, if *p*-nitrophenylhydrazine be employed, the hydrazino-compound (XXVII) represents the final product, since a hydrazone cannot be prepared from it. Further, it is not surprising that the normal hydrazone (XXVIII) can be obtained by the use of the hydrazine hydrochloride, since this would obviously have little tendency to react additively at the ethylene linking. But it is remarkable that the hydrazone (XXVIII) is converted into a pyrazoline (XXIX) by means of sodium hydroxide (or hydrochloric acid), since alkali causes the rearrangement of the original ketone into a chromanone.

Again, the *p*-nitrophenylhydrazone (XXX) of this chromanone is obtained by the use of hot glacial acetic acid—a reagent which, in the case of the compound (XXV), facilitates pyrazoline formation. The fineness of the balance between the tendencies to chromanone and pyrazoline formation will be apparent from the fact that from five experiments carried out with glacial acetic acid the chromanone was obtained in three, the pyrazoline in two, cases. The easy formation of a hydrazone from the azo-compound corresponding with the non-reactive hydrazino-compound (XXVII) is also noteworthy.

[14] K. von Auwers, *Ber.*, 1920, **53**, [*B*], 2271; *A.*, i, 118.

[15] K. von Auwers and H. Voss, *ibid.*, 1909, **42**, 4411; *A.*, 1910, i, 70; E. P. Kohler, *Amer. Chem. J.*, 1909, **42**, 775; *A.*, 1909, i, 938.

[16] K. von Auwers and E. Lämmerhirt, *Ber.*, 1921, **54**, [*B*], 1000; *A.*, i, 464.

Me⟨ ⟩CO·CH:CMe₂ / OH → Me⟨ ⟩C(N·NHPh)·CH₂·CMe₂·NH·NHPh / OH

(XXVI.)

Me⟨ ⟩CO·CH₂·CMe₂·NH·NH·C₆H₄·NO₂ / OH

(XXVII.)

Me⟨ ⟩C(N·NH·C₆H₄·NO₂)·CH₂·CMe₂ / O

(XXX.)

Me⟨ ⟩—C⟨CH₂·CMe₂ / N—N·C₆H₄·NO₂⟩OH $\underset{\text{NaOH}}{\overset{\text{HCl or}}{\longleftarrow}}$ Me⟨ ⟩C(N·NH·C₆H₄·NO₂):CH:CMe₂ / OH

(XXIX.) (XXVIII.)
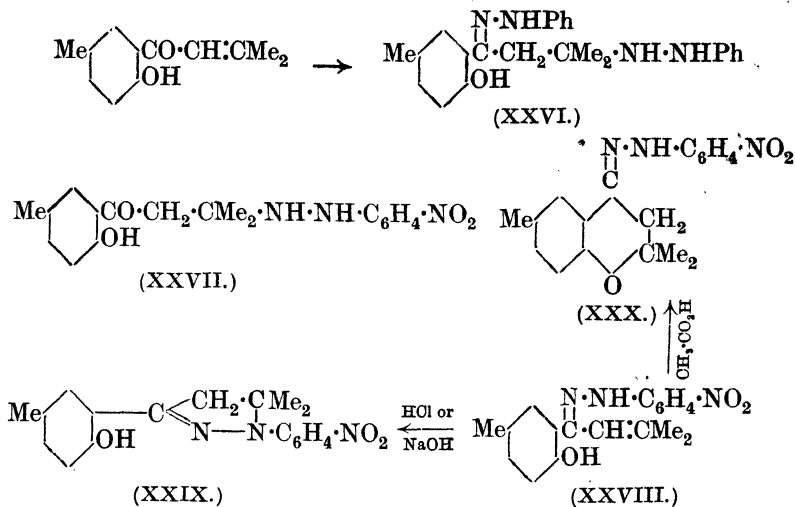
The syntheses of azines from picryl chloride by condensation with o-amino-phenols or -thiophenols, or o-phenylenediamines, and subsequent treatment with alkali, are well known, and can be applied to the case of 1-chloro-2 : 6-dinitrobenzene.[17] But 2 : 4-dinitro-2'-hydroxydiphenylamine (XXXI) is converted into an oxazine (XXXII) only with much difficulty,[18]

O₂N⟨ ⟩(NO₂)—NH—⟨ ⟩(HO) → O₂N⟨ ⟩(NH)⟨ ⟩ / O

(XXXI.) (XXXII.)

⟨ ⟩(NO₂)(NO₂)—NH—(Ph₂HC)⟨ ⟩
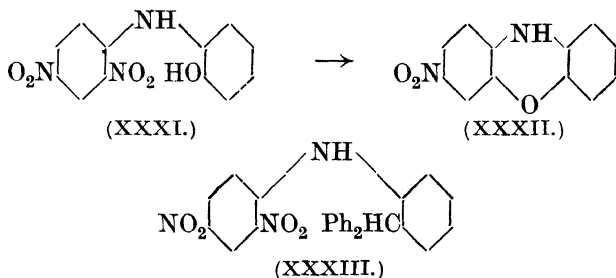
(XXXIII.)

whilst 2 : 4-dinitro-2'-benzhydryldiphenylamine (XXXIII) could not be converted into a nitrodiphenylcarbazine,[19] and a nitrophenyl-dihydrophenazine could not be obtained from 2 : 4-dinitro-2'-anilinodiphenylamine.[20] Yet the 2 : 6-, and, of course, the 2 : 4 : 6-trinitro-analogues are in each case amenable to condensation. Here again, therefore, the position of a substituent is a considerable factor in determining the result.

[17] F. Ullmann and E. Kuhn, *Annalen*, 1909, **366**, 79; *A.*, 1909, i, **473**.

[18] F. Kehrmann and (Miss) M. Ramm, *Ber.*, 1920, **53**, [B], 2265; *A.*, i, 128.

[19] F. Kehrmann, (Miss) M. Ramm, and Ch. Schmajewski, *Helv. Chim. Acta*, 1921, **4**, 538; *A.*, i, 600.

[20] K. Kehrmann and J. Effront, *ibid.*, 517; *A.*, i, 601.

The operation of yet another factor on the stability of cyclic compounds seems to be distinguishable in the course of the condensation of 2-thiolbenzoic acid with compounds containing a reactive methylene group in presence of sulphuric acid. For example, the usual product from acetylacetone is 3-oxy(1-)thionaphthen (XXXV). Its 2-acetyl derivative (XXXIV) is obtained only under mild conditions of reaction, whilst the 2 : 2-diacetyl derivative (XXXVI), of which the initial formation is to be presumed, cannot be isolated : [21]

$$C_6H_4{<}^{SH}_{CO\cdot OH} \rightarrow \left[C_6H_4{<}^{S-}_{CO}{>}C(CO\cdot CH_3)_2 \right] \rightarrow$$
$$(XXXVI.)$$

$$C_6H_4{<}^{S-}_{CO}{>}CH\cdot CO\cdot CH_3 \rightarrow C_6H_4{<}^{S-}_{CO}{>}CH_2$$
$$(XXXIV.) \qquad\qquad (XXXV.)$$
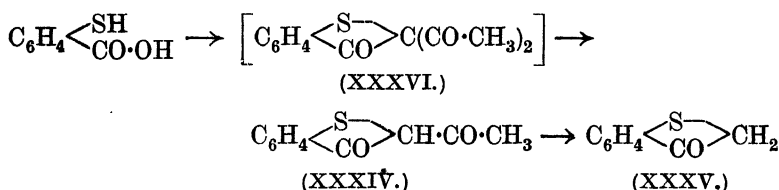
Since 2-acetyl-3-oxy(1-)thionaphthen is a tautomeric substance, the decomposition of the diacetyl derivative would appear to be due to its tendency to acquire a tautomeric hydrogen atom.[22] Further, since the alcoholic solution of the monoacetyl derivative is coloured green by ferric chloride, the compound evidently exists to some extent in the enolic form, which, in the case of ethyl acetoacetate itself, is known easily to undergo acid hydrolysis. The 3-oxythionaphthens are intermediate in their chemical properties between the coumaranones and the hydrindones.[23]

Ring Transformations.

A number of instances have been recorded in recent years of the transformation of the five-membered ring of isatin into a six-membered ring. In addition to those already noticed in these Reports,[24] reference may be made to the formation of cinchonic acids by condensation of isatin with compounds, such as phenyl-acetic and malonic acids,[25] which contain a reactive methylene group. The products (XXXVII) and (XXXVIII) are obtained in the cases mentioned. Since the acid (XXXIX) is obtained from N-methyl-

[21] S. Smiles and E. W. McClelland, T., 1921, **119**, 1810; compare A. M. Hutchison and S. Smiles, T., 1912, **101**, 570.

[22] Compare F. B. Thole and J. F. Thorpe, T., 1911, **99**, 2183.

[23] K. von Auwers and W. Thies, Ber., 1921, **54**, [B], 2285; A., i, 120.

[24] Ann. Reports, 1919, **16**, 112; also G. Heller and P. Jacobsohn, Ber., 1921, **54**, [B], 1107; A., i, 440.

[25] W. Borsche and W. Jacobs, ibid., 1914, **47**, 354; W. Borsche and W. Sander, ibid., 2815; W. Borsche and R. Meyer, ibid., 1921, **54**, [B], 2841; A., 1914, i, 322; 1915, i, 299; 1922, i, 53.

isatin, the formation of an analogous intermediate product from isatin is assumed :

(XXXVII.)   (XXXVIII.)

(XXXIX.)
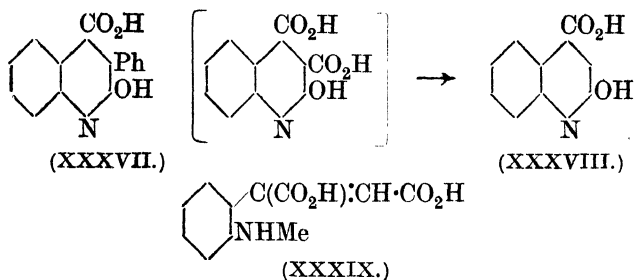
The conversion of isatin into its β-oxime and 3-nitroquinoline-carboxylic acid by condensation with methazonic acid in presence of alkali [26] also involves at some stage the opening of the indole ring :
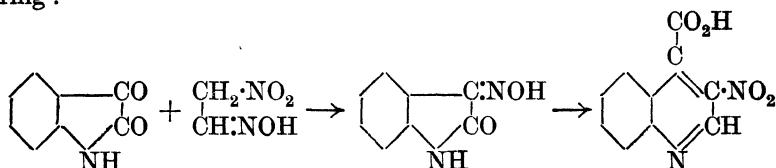
The reverse process—transformation of a pyridine into a pyrrole ring—has now been observed for the first time. Ethyl 2 : 6-dimethyl-4-cyanomethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate (XL) is converted into ethyl 5-methyl-3-cyanomethylpyrrole-2-carboxylate (XLI) under the influence of boiling alcoholic potassium hydroxide :

(XL.)   (XLI.)   (XLII.)
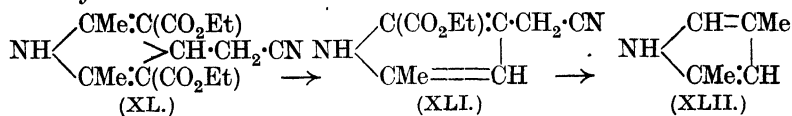
The reaction is dependent on the presence of the cyanogen group, since ethyl 2 : 4 : 6-trimethyl-1 : 4-dihydropyridine-3 : 5-dicarboxylate does not undergo a similar change. The constitution of the product (XLI) is established by its eventual conversion into 2 : 4-dimethylpyrrole (XLII),[27] but it will be noticed that this is not conclusive in respect of the carbethoxy-group.

Structural Isomerism.

A polemical discussion [28] has arisen in regard to the existence

[26] B.A.S.F., D.R.-P. 335197; A., i, 517.

[27] E. Benary, Ber., 1920, 53, [B], 2218; A., i, 127.

[28] A. Hantzsch, ibid., 1921, 54, [B], 1221, 1257; G. Heller, ibid., 2214; A., i, 597, 598.

of the various alleged isomerides of isatin.[29] As the matter is still in debate a fuller account is postponed, but an interesting point has emerged which bears on Hartley's classical measurements of the absorption spectrum of O-methylisatin. It was overlooked that this compound rapidly isomerises in solution. This was perhaps fortunate, since the close resemblance of the absorption of this compound in freshly prepared solutions to those of isatin and its N-methyl derivative might have delayed recognition of a method which has since proved of such value in connexion with the study of tautomeric compounds.

A further investigation of the *iso*isatogens, derived from the more highly coloured isatogens by treatment with alcoholic hydrogen chloride, has shown that they have the molecular weight demanded by the formula (XLIII) originally proposed for them,[30] lack the oxidising properties of the isatogens, and are not phenolic, but exhibit ketonic properties. Their reconversion into the isatogens (XLIV) by heating them alone or in glacial acetic acid solution or, most effectively, with phenylcarbimide, also indicates the intimate relationship suggested by the formulæ : [31]

$$\underset{\text{(XLIII.)}}{\text{structure with --CO, CR, N--O}} \quad \underset{\text{alc.HCl}}{\overset{\text{heat}}{\rightleftarrows}} \quad \underset{\text{(XLIV.)}}{\text{structure with --CO, CR, N, O}}$$
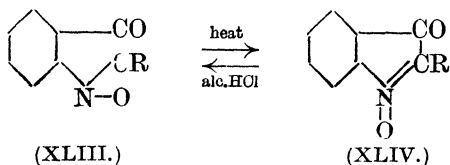
The formula (XLV) for the furoxans has been defended [32] on the ground that there is evidence of asymmetry in these compounds. Thus, the amide of furoxandicarboxylic acid is decomposed,

$$\underset{\text{(XLV.)}}{X \cdot C - C \cdot Y / N \quad N > O / O} \qquad \underset{\text{(XLVI.)}}{HO_2C \cdot C - C \cdot OH / NOH \quad NOH} \leftarrow \qquad \underset{}{HO_2C \cdot C - CH / N \quad N > O / O}$$

$$\uparrow$$

$$\underset{\text{(XLVII.)}}{NC \cdot C \cdot CO \cdot NH_2 / NO \cdot OH} \leftarrow \underset{}{CH - C \cdot CO \cdot NH_2 / N \quad N > O / O} \leftarrow \underset{}{H_2N \cdot OC \cdot C - C \cdot CO \cdot NH_2 / N \quad N > O / O}$$
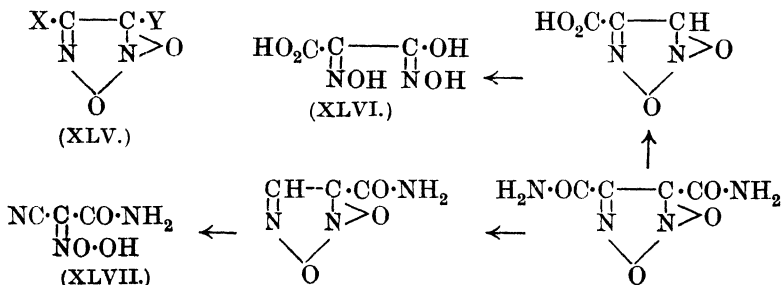
[29] G. Heller, *Ber.*, 1907, **40**, 1291; 1916, **49**, 2757; 1917, **50**, 1199; 1918, **51**, 180, 1270; 1919, **52**, 437; 1920, **53**, [*B*], 1545; A., 1907, i, 442; 1917, i, 219, 708; 1918, i, 235; 1919, i, 36, 282; 1920, i, 766.

[30] Compare *Ann. Reports*, 1919, **15**, 109.

[31] P. Rüggli and A. Bolliger, *Helv. Chim. Acta*, 1921, **4**, 626, 637; *A.*, i, 811, 812.

[32] H. Wieland, *Annalen*, 1921, **424**, 107; *A.*, i, 605.

according to the conditions employed, into *iso*nitrosohydroxamic acid (XLVI),[33] or into fulminuric acid (XLVII).[34] Although all the methods of formation of phenylfuroxan, as would be expected, yield the same product (XLVIII) rather than (XLIX), they, and also the action of nitrogen trioxide on phenylacetylene, first give rise to an unstable isomeride of phenylfuroxan, which passes into the known derivative, and which may possibly correspond with the formula (L).[35]

$$\begin{array}{ccc} \text{(XLVIII.)} & \text{(XLIX.)} & \text{(L.)} \end{array}$$
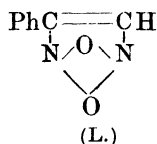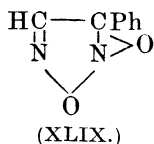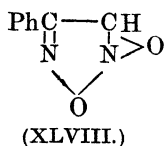
An interesting form of desmotropy has been observed with both di- and tri-2-quinolylmethanes. These compounds, which are prepared by the interaction of suitable quantities of quinaldine and 2-chloroquinoline, each exist in two interconvertible modifications. Thus, di-2-quinolylmethane, when first prepared, is a mixture of the colourless compound (LI) with a small amount of a red isomeride (LII), which is decolorised by bromine and in alcoholic solution is slowly converted into the colourless form, more rapidly in presence of alkali. The same two series of salts—coloured monoacidic and colourless diacidic—are obtainable from each. *N*-Methyl-2-quinolylenequinaldine (LIII), prepared by methylation with methyl iodide or sulphate, is also red and stable.[36]

(LI.) (LII.)

(LIII.)
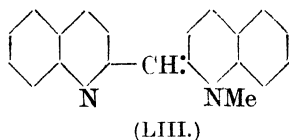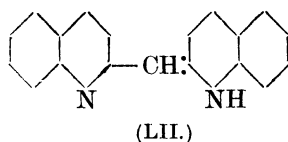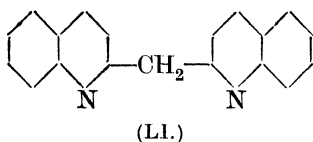
A reference to isomerism among thiophen derivatives will be found on p. 125.

[33] H. Wieland, *Annalen*, 1909, **367**, 56; *A.*, 1909, i, 609.

[34] C. Ulpiani, *Gazzetta*, 1905, **35**, ii, 7; *A.*, 1905, i, 750.

[35] Compare A. G. Green and F. M. Rowe, *T.*, 1912, **101**, 2452; 1914, **105**, 897, 2023.

[36] G. Scheibe and E. Rossner, *Ber.*, 1920, **53**, [*B*], 2064; G. Scheibe, *ibid.*, 1921, **54**, [*B*], 786; *A.*, i, 62, 451.

Stereoisomerism.

Further attempts have been recorded to prepare tervalent nitrogen compounds, the configuration of which would be likely to prove sufficiently stable to permit their resolution. One investigation,[37] in which the following series of reactions was attempted,

was unsuccessful because, in place of the desired 1-β-iodoethyl-benziminazole (LIV.), a polymeride, resulting from intermolecular quaternary ammonium iodide formation, was obtained. The statement that a side-chain could not be introduced into tetrahydroquinoxaline is at variance with an account [38] of the preparation of 1:4-*endo*-methylene-, -ethylene-, and -trimethylene-6-methyltetrahydroquinoxalines (LV, LVI, and LVII) by treatment

of tetrahydroquinoxaline with methylene iodide or formaldehyde, ethylene dibromide, and trimethylene dibromide respectively.

Experiments on the synthesis of di-*N*-methyldi-α-pyrrolidyl-methane (LVIII), obtained as a degradation product of cusk-hygrine,[39] have yielded notable results.[40] Di-α-pyrryl ketone (LIX) is best prepared by the action of carbonyl chloride on magnesium

[37] J. Meisenheimer and B. Wieger, *J. pr. Chem.*, 1921, [ii], **102**, 45; *A.*, i, 739.

[38] T. S. Moore and (Miss) I. Doubleday, *T.*, 1921, **119**, 1170.

[39] Compare *Ann. Reports*, 1920, **17**, 126.

[40] K. Hess and F. Anselm, *Ber.*, 1921, **54**, [B], 2310; *A.*, i, 881.

pyrryl bromide or, less satisfactorily, potassium pyrrole,[41] and has also been obtained from α-pyrroyl chloride and magnesium pyrryl bromide.[42] By catalytic reduction, di-α-pyrrolidylmethane is obtained, and this is converted into the desired compound by treatment with formaldehyde.

Both these pyrrolidine derivatives, however, are mixtures of stereoisomerides. The *N*-methyl compound furnishes three distinct methiodides, which differ from the two now found to be obtainable from the degradation product of cuskhygrine. It is tentatively suggested that the existence of these five isomerides is another illustration of stereoisomerism connected with the two nitrogen atoms, which, in conjunction with the two asymmetric carbon atoms, would result in the existence of two meso- and four racemic compounds. If this be so, it is interesting that the products of natural synthesis should differ in configuration from those obtained in the laboratory.

Asymmetric Rearrangement.

An automatic resolution of the quinidine salt of *r*-hydrocarbo-styril-3-carboxylic acid (LX) occurs when this is prepared in methyl alcoholic solution from its components, since the sole product, which is obtained quantitatively, is that derived from the *d*-acid. The result is due to the enolisation of the acid and the relatively sparing solubility of the salt of the *d*-acid :

Crystalline *d*-acid salt.　⟵　*d*-Acid salt solution　　*l*-Acid salt solution
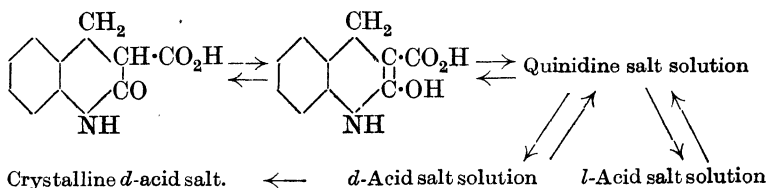
The result only differs from an asymmetric synthesis in that throughout no change of molecular weight is involved, and is therefore termed an "asymmetric rearrangement."[43] Confirmation of this explanation is derived from the gradual racemisation of the free active acid, which commences immediately the acid is dissolved. 2-*o*-Carboxybenzylhydrindone (LXI) undergoes a similar resolution through its brucine salt.[44] The formation of an inactive sulphone from the optically active forms of α-thiodi-propionic acid [45] (LXII) is possibly due to similar causes.

[41] G. Ciamician and P. Magnaghi, *Ber.*, 1885, **18**, 419; *A.*, 1885, 809.

[42] B. Oddo, *Gazzetta*, 1920, **50**, ii, 258; *A.*, i, 129.

[43] H. Leuchs, *Ber.*, 1921, **54**, [*B*], 830; *A.*, i, 442.

[44] H. Leuchs and J. Wutke, *ibid.*, 1913, **46**, 2425; *A.*, 1913, i, 974.

[45] J. M. Lovén and R. Ahlberg, *ibid.*, 1921, **54**, [*B*], 227; *A.*, i, 223.

(LXI.)

$(CHMe \cdot CO_2H)_2S \longrightarrow (CHMe \cdot CO_2H)_2SO_2$
(LXII.)
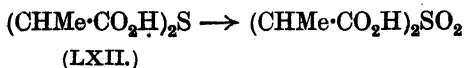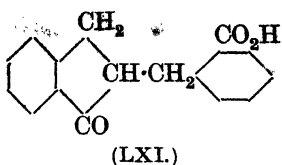
Alkylation.

Alkylation represents one of the most valued and general methods of investigation at the disposal of the organic chemist, and corresponding importance attaches to inquiries as to the variation to be obtained in the results by modification of the experimental conditions.

By the action of methyl iodide on either 2-aminopyridine or its sodium derivative (LXIII), two methyl derivatives are obtained. 1-Methyl-2-pyridoneimide (LXIV) is the chief product in the former case, whilst 2-methylaminopyridine (LXV) predominates in the latter :

(LXIII.)   (LXIV.)   (LXVI.)   (LXV.)
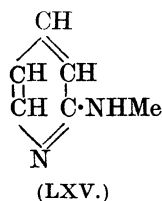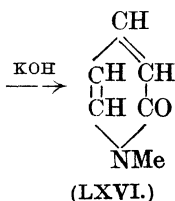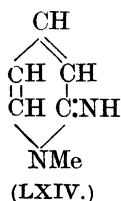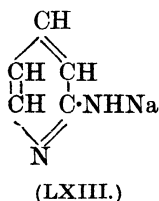
The structure of the imino-derivative is proved by its hydrolysis with alkali to ammonia and 1-methyl-2-pyridone (LXVI).[46] Its stability towards dilute acids differentiates it from ordinary ketimines, but it may be observed that the same property is exhibited by the analogously constituted amidines.[47] Interesting as these results are, it may be doubted whether they justify the idea that they are evidence of " the tautomerism of α-aminopyridine," and the same applies to other cases of a similar kind.[48] Thus, the formation of the ketimine is possibly the outcome of reactions closely resembling those by which ethyl α-acetylbutyrate is obtained from ethyl β-aminocrotonate : [49]
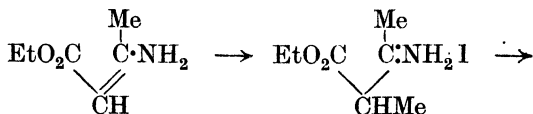
[46] A. E. Tschitschibabin, R. A. Konowalowa, and A. A'. Konowalowa, *Ber.*, 1921, **54**, [*B*], 814; *A.*, i, 450.

[47] Compare, for example, H. von Pechmann, *ibid.*, 1895, **28**, 2368; *A.*, 1896, i, 31.

[48] A. E. Tschitschibabin, *ibid.*, 1921, **54**, [*B*], 822; *A.*, i, 451.

[49] R. Robinson, *T.*, 1916, **109**, 1039.

$$\begin{matrix} & \text{Me} & & & & \text{Me} \\ \text{EtO}_2\text{C} & \text{C:NH} & \longrightarrow & \text{EtO}_2\text{C} & \text{CO} \\ & \diagdown\diagup & & & \diagdown\diagup \\ & \text{[CHMe} & & & \text{CHMe} \end{matrix}$$
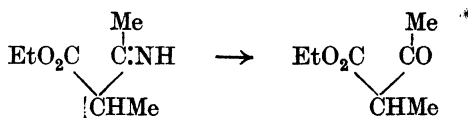
The analogy between the behaviour of the two amino-compounds is not, however, complete, since the crotonate and its sodium derivative do not furnish a mixture of products on alkylation, and ethyl β-amino-α-methylcrotonate, derived from the sodium derivative, does not correspond with the main product from 2-pyridylsodamide. But it must also be remembered that the tertiary nitrogen atom of 2-aminopyridine, unlike the methine carbon atom in ethyl β-aminocrotonate, shares with the amino-group the capacity for combination with the halogen atom of the alkyl iodide.

The danger of basing conclusions solely on the results of alkylation is strikingly illustrated by experiments in the indazole series.[50] The following may serve as illustrations of the variety of results obtained. From silver indazole (LXVII) and suitable alkyl iodides at the ordinary temperature, 2-methyl, 1-benzyl, and 1-allyl derivatives were obtained, but increasing amounts of the 1-methyl isomeride resulted as the temperature of reaction was raised. The direct interaction of indazole with alkyl iodides at 100° gave rise to mixtures, in which the 2-derivatives predominated. By the use of one sample of benzyl chloride at 140°, 1-benzylindazole was produced, whilst another sample consistently yielded the 2-derivative. Alkylation in presence of boiling alcoholic sodium hydroxide usually furnished approximately equal amounts of the 1- and 2-isomerides.

$$\begin{matrix} & \diagup\diagdown & \text{CH} & \diagdown \\ \Big| & & \Big| & \diagup\text{NAg} \\ & \diagdown\diagup & \text{N} \diagup \end{matrix}$$

(LXVII.)
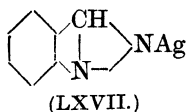
A detailed study [51] of the methylation of uric acid shows that this also is a somewhat complicated process. Conductivity measurements of the various methyluric acids show that the acidity of the hydrogen atoms in positions 3, 9, 1, and 7 diminishes in the order given, the last two being so feebly acid that uric acid is dibasic. Alkylation of the dry lead or potassium salts with alkyl iodides corresponds with that of ethyl acetoacetate, and results in the formation first of 3-, then of 9-methyl derivatives, and the same applies to alkyl derivatives in which these positions are free :

$$\text{—N:C(OK)—} \longrightarrow \text{—NMe·CO—.}$$
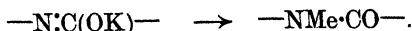
[50] K. von Auwers, *Ber.*, 1919, **52**, 1330; K. von Auwers and R. Dereser, *ibid.*, 1340; K. von Auwers and W. Schaich, *ibid.*, 1921, **54**, [*B*], 1738; *A.*, 1919, i, 455, 456; 1921, i, 806.

[51] H. Biltz and (Miss) L. Herrmann, *ibid.*, 1921, **54**, [*B*], 1676; *A.*, i, 691.

By the use of methyl sulphate and alkaline solutions, however, the least acidic hydrogen atoms are first replaced. Thus the respective products from 3 : 7-, 7 : 9-, and 3 : 9-dimethyluric acids are 1 : 3 : 7-, 1 : 7 : 9-, and equal proportions of 1 : 3 : 9- and 3 : 7 : 9-trimethyluric acids. Probably quaternary methyl metho-sulphates are first produced, and this occurs by preference at the most basic (least acidic) nitrogen atom of the uric acid molecule :

$$-\text{NH·CO}- \ \longrightarrow \ -\text{NH·CO}- \ \longrightarrow \ -\text{NMe·CO}-$$
$$\text{Me}\diagup\diagdown\text{SO}_4\text{Me}$$
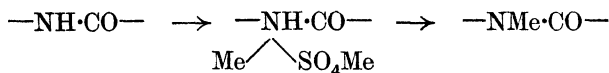
But this explanation does not seem to meet all the facts, since, by treatment of uric acid with methyl sulphate, a considerable proportion of 1 : 3-dimethyluric acid is produced. It would there-fore appear that other factors are in operation, as, indeed, is recognised to be the case when·methyl iodide is used in place of the sulphate. The mode of action of formaldehyde appears to correspond with that of methyl sulphate. The use of diazo-methane [52] yields noteworthy results. Although compounds in which the 3- and 9-positions are already alkylated do not react, substitution also occurs in the 1- and 7-positions when either of the former positions is free. Further, 8- and 2-alkoxy-derivatives are formed in certain cases, but only one such group is produced. Thus uric acid gives rise to 8-methoxy-2 : 6-dihydroxy-1 : 3 : 7-trimethylpurine, which changes at 200° into 1 : 3 : 7 : 9-tetramethyl-uric acid.

Heterocyclic Arsenic Compounds.

The arsenic analogues of phenyl-piperidine and -pyrrolidine were the only heterocyclic arsenic compounds known [53] until it was observed that phenarsazine chloride (LXVIII) is readily obtained by boiling a mixture of arsenious chloride with diphenyl-amine : [54]

(LXVIII.)

$$\text{NH}\!<^{\text{C}_6\text{H}_4}_{\text{C}_6\text{H}_4}\!\!>\!\text{AsO·OH}$$

(LXIX.)

$$\text{C}_6\text{H}_4\!\ll^{\text{As}}_{\text{N}}\!\!>_6\text{CH}_4$$

(LXX.)
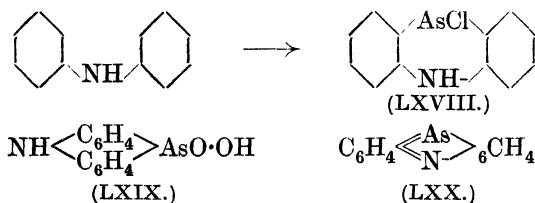
The product resembles diphenylarsenious chloride both in its sternutatory and in its chemical actions. The corresponding oxide (but not the hydroxide), methyl ether, acetate, and sulphide

[52] H. Biltz and F. Max, *Ber.*, 1920, 53, [B], 2327; *A.*, i, 131.
[53] Compare *Ann. Reports*, 1916, 13, 131.   [54] D.R.-P. 281049 (1915).

are easily obtained and reconverted into the chloride, whilst phenarsazinic acid (LXIX) is obtained by oxidation. Phenarsazine (LXX), best obtained by heating phenarsazine methyl ether, is an orange-yellow compound, characterised by the special avidity, reminiscent of the ketens, with which it is reconverted 'into phenarsazine derivatives by direct combination with suitable reagents.[55] Further, arsanthrene (LXXI) has been prepared [56] by the reactions indicated in the following scheme :

(LXXI.)   (LXXII.)
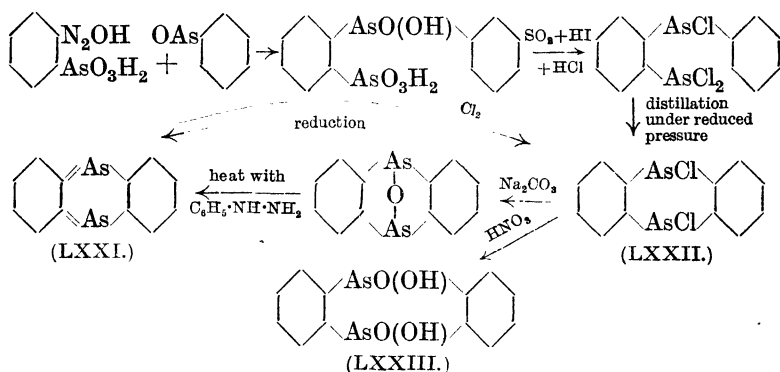
(LXXIII.)

The orange-yellow product, or its chloride (LXXII), is oxidised by nitric acid to arsanthrenic acid (LXXIII).[55]

Some Heterocyclic Sulphur Compounds.

Interesting results have been obtained by the action of various thio-derivatives on diazo-compounds. Thus, diphenyldiazomethane and thiobenzophenone yield tetraphenylethylene sulphide,[57] which could not be oxidised to the corresponding sulphone,[58] and is decomposed by heat into tetraphenylethylene and sulphur :
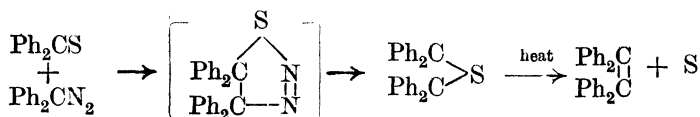
From thiocarbonyl chloride and diphenyldiazomethane, *as*-dichloro-diphenylethylene sulphide (LXXIV) is first obtained, but gradually

[55] H. Wieland and W. Rheinheimer, *Annalen*, 1921, **423**, 1; *A.*, i, 371.

[56] L. Kalb, *ibid.*, 39; *A.*, i, 375.

[57] H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 833; *A.*, i, 43.

[58] Compare H. Staudinger and F. Pfenninger, *Ber.*, 1916, **49**, 1941; *A.*, 1916, i, 852.

changes into *as*-dichlorodiphenylethylene and sulphur.[59] Its chlorine atoms are not reactive, but the product (LXXV) obtained from benzoylphenyldiazomethane and thiocarbonyl chloride is decomposed by the moisture of the atmosphere into the compound (LXXVI), from which deoxybenzoin and sulphur are produced by the action of alkali :

$$
\underset{\text{(LXXIV.)}}{\overset{Ph_2C}{\underset{Cl_2C}{}}\!\!>S} \qquad \underset{\text{(LXXV.)}}{\overset{PhC-CCl_2}{\underset{PhC-O}{\|}}\!\!>S} \;\rightarrow\; \underset{\text{(LXXVI.)}}{\overset{PhC-CO}{\underset{PhC-O}{\|}}\!\!>S} \;\rightarrow\; \underset{}{\overset{PhCH_2}{\underset{PhCO}{}}} + CO_2 + S
$$
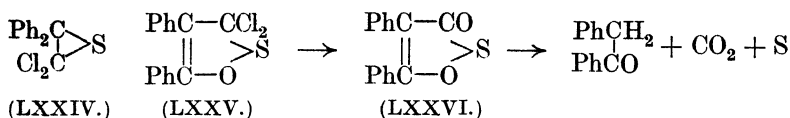
Five-membered Heterocyclic Structures.

It has long been known that the entrance of substituents into the carbon system of the pyrrole ring, whether directly or in consequence of molecular rearrangement of *N*-substituted derivatives, normally occurs in the 2-position. Evidence is, however, accumulating that 3-derivatives may also be formed if the 2-position is not free. Thus, by the action of sodium ethoxide on 2 : 3 : 5-trimethylpyrrole at 200°, its 4-ethyl derivative (phyllopyrrole) (LXXVII), was synthesised.[60] Again, 1-formyl-2 : 5-dimethylpyrrole suffers rearrangement at 200° in presence of zinc chloride into 3-aldehydo-2 : 5-dimethylpyrrole (LXXVIII) :

$$
\underset{\text{(LXXVII.)}}{\overset{\text{EtC}-\!\!-\text{CMe}}{\underset{\text{MeC}\;\;\text{CMe}}{\underset{\diagdown\!\diagup}{}}}\;\;\;\;\overset{}{\underset{\text{NH}}{}}} \qquad \underset{\text{(LXXVIII.)}}{\overset{\text{HC}-\!\!-\text{C·CHO}}{\underset{\text{MeC}\;\;\text{CMe}}{\underset{\diagdown\!\diagup}{}}}\;\;\;\;\overset{}{\underset{\text{NH}}{}}} \qquad \underset{\text{(LXXIX.)}}{\overset{\text{HC}-\!\!-\text{C·CO·CH}_3}{\underset{\text{MeC}\;\;\text{CMe}}{\underset{\diagdown\!\diagup}{}}}\;\;\;\;\overset{}{\underset{\text{S}}{}}}
$$
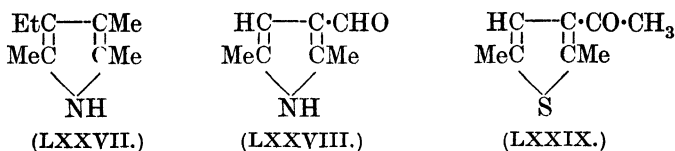
Similarly, in the thiophen series, 2-thienyl ketones are formed by the action of acid anhydrides on thiophen.[61] But, from 2 : 5-dimethylthiophen 2 : 5-dimethyl-3-thienyl methyl ketone (LXXIX) is obtained, although the reaction proceeds less easily.[62] Further, it had been hoped that the formation of thienylmercurichlorides from thiophens [63] by the action of mercuric chloride would afford a means of distinguishing 1- from 2-derivatives. This is, however, not the case, since the additive compound (LXXX) has been obtained from 2 : 5-dimethylthiophen, corresponding with that formed by the 2 : 4-isomeride (LXXXI) : [64]

[59] H. Staudinger and J. Siegwart, *Helv. Chim. Acta*, 1920, **3**, 840; *A.*, i, 43.

[60] H. Fischer and E. Bartholomaus, *Ber.*, 1912, **45**, 466; *A.*, 1912, i, 297.

[61] *Ann. Reports*, 1917, **14**, 124.

[62] W. Steinkopf and J. Schubert, *Annalen*, 1921, **424**, 1; *A.*, i, 579.

[63] *Ann. Reports*, 1917, **14**, 123.

[64] W. Steinkopf, *Annalen*, 1921, **424**, 23; *A.*, i, 630.

$$\begin{array}{ccc} \text{HC}\!-\!\text{CMe·OH} & \text{HC}\!-\!\text{CH·HgCl} & \text{CH}\!=\!\text{CH} \\ \text{MeC}\quad\text{CH·HgCl}, \text{HgCl}_2 & \text{MeC}\quad\text{CMe·OH}, \text{HgCl}_2 & \\ \diagdown\diagup & \diagdown\diagup & \\ \text{S} & \text{S} & \text{S} \\ (\text{LXXX.}) & (\text{LXXXI.}) & (\text{LXXXII.}) \end{array}$$
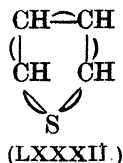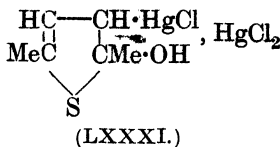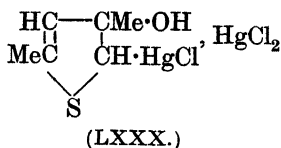
These compounds also have the interest that they render probable the formation of such compounds in general as a preliminary to the mercurichlorides proper. These, with the mercurithiocyanates obtained from them by double decomposition with sodium thiocyanate, can be used to characterise the alkyl and aryl thiophens. By this method, an interesting case of isomerism has been discovered. 2 : 5-Diphenylthiophen, m. p. 152°, from diphenacyl and phosphorus pentasulphide,[65] gives the same mercury derivatives as the isomeric product, m. p. 119°, obtained from anhydrotriacetophenone disulphide.[66] The result recalls the existence of two forms of dinitrothiophen, of which one is convertible into the other.[67]

Thiophen may be mono- or di-halogenated by suitable treatment with aceto-chloro- or -bromo-amide.[68] Although this reaction indicates a certain degree of unsaturation,[69] it is suggested that the formula (LXXXII) offers the best expression of the properties of thiophen. No experiments are described on the attempted halogenation of 2 : 5-substituted thiophens by this method.

Recognition of the fact that the therapeutic value of ichthyol oils is due to the presence of alkylthiophens [70] has stimulated interest in these compounds. The propyl and isopropyl derivatives have been prepared by the classical methods,[71] but these and methods depending on the action of sulphur on olefines [72] or of iron pyrites on butadienes [73] are inferior to that which consists in the reduction of the corresponding ketones by Clemmensen's method.[74]

Hydrazine is not a suitable reagent for the reduction of indigotin to indigo-white, since it has no effect by itself, whilst in presence of alkali reduction occurs, but the solution gradually loses its dyeing

[65] S. Kapf and C. Paal, Ber., 1888, 21, 3058; A., 1888, 839.

[66] E. Baumann and E. Fromm, ibid., 1897, 30, 117; A., 1897, i, 191.

[67] V. Meyer, " Die Thiophengruppe," p. 98.

[68] W. Steinkopf and A. Otto, Annalem, 1921, 424, 61; A., i, 579.

[69] Compare A. Wohl, Ber., 1921, 54, [B], 476; A., i, 317.

[70] H. Scheibler, Arch. Pharm., 1920, 258, 84.

[71] H. Scheibler and M. Schmidt, Ber., 1921, 54, [B], 139; A., i, 191.

[72] E. Baumann and E. Fromm, ibid., 1895, 28, 891; A., 1895, i, 337.

[73] W. Steinkopf, Annalen, 1914, 403, 11; A., 1914, i, 425.

[74] W. Steinkopf and J. Schubert, loc. cit.

properties. If air be then drawn through the solution, a yellow precipitate will separate, to which the constitution (LXXXIII) is attributed. "Thioindigo" under similar conditions is converted into a leuco-compound, from which it is regenerated by the action of air.[75] The colour of indigotin and its derivatives has been discussed from the points of view both of its origin,[76] and of its relation to constitution.[77]

(LXXXIII.)   (LXXXIV.)
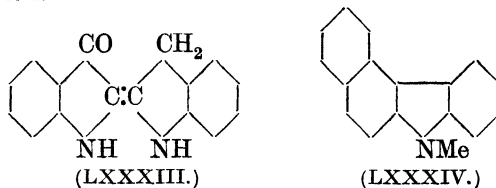
The formation of *N*-methylnaphthaphenocarbazole (LXXXIV) by the action of *as*-phenylmethylhydrazine on 2-hydroxy-3-naphthoic acid in presence of sodium hydrogen sulphite[78] is important in that it confirms the view that the Bucherer-Lepetit reaction proceeds by formation of a bisulphite additive compound of the ketonic form of naphthols rather than of a sodium naphthylsulphite by condensation of the naphthol with the bisulphite.

The oxidation of carbazole with potassium permanganate results in the formation of three products, of which two have been identified as dicarbazyls, although their precise constitution is at present indefinite.[79] By the use of silver oxide, two products are obtained, of which one appears to be *NN*-dicarbazyl (LXXXV), and is interesting because, although colourless, it gives rise to reddish-brown solutions with a blue fluorescence. The freezing points of these in benzene indicate a dissociation varying from 20—40 per cent. directly with the concentration, but the compound does not yield a peroxide or decolorise iodine solution.[80]

(LXXXV.)   (LXXXVI.)   (LXXXVII.)
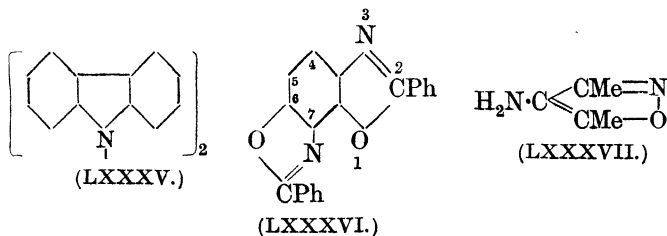
[75] W. Borsche and R. Meyer, *Ber.*, 1921, **54**, [*B*], 2854; *A.*, 1922, i, 55.

[76] R. Robinson, *J. Soc. Dyers and Col.*, 1921, **37**, 77; *A.*, i, 452.

[77] J. Martinet, *Rev. Gén. Mat. Col.*, 1921, **25**, 17; *A.*, i, 273.

[78] P. Friedländer, *Ber.*, 1921, **54**, [*B*], 620; *A.*, i, 443.

[79] W. H. Perkin, jun., and S. H. Tucker, *T.*, 1921, **119**, 216.

[80] G. E. K. Branch and J. F. Smith, *J. Amer. Chem. Soc.*, 1920, **42**, 2405; *A.*, i, 56.

A study of the relationship between the constitution of benz-oxazoles and their visible fluorescence [81] has shown that this occurs only when the 2-position is occupied by an aromatic group and a methyl or a salt-forming (for example, hydroxyl) group is present in the 6-position. Substitution in the 4-, 5-, or 7-position, however, may inhibit the fluorescence, as in the case of the compound (LXXXVI).

The property of diazotisability has been shown in recent years to be shared with aromatic amines by a number of heterocyclic compounds, to which 4-amino-3 : 5-dimethyl*iso*oxazole (LXXXVII) must now be added.[82]

Two papers deal with the formation of double compounds of antipyrine with metallic salts.[83]

The Pyrone Group.

A straightforward synthesis of 2 : 6-dimethylpyrone consists in the gradual addition of sulphuric acid to an ice-cold mixture of acetone and acetic anhydride, although the yield amounts to only 4 per cent. : [84]

$$O{<}^{CO \cdot CH_3}_{CO \cdot CH_3} + {}^{CH_3}_{CH_3}{>}CO \longrightarrow O{<}^{CMe:CH}_{CMe:CH}{>}CO$$
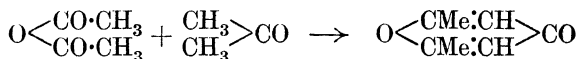
Similarly, by the use of methyl ethyl ketone, 2 : 3 : 6-trimethyl-pyrone is obtained.

A synthesis of meconic acid has been achieved [85] by the bromination of ethyl acetonyldioxalate, followed by spontaneous dehydration of the primary product (LXXXVIII) into ethyl 3-bromo-chelidonate, from which potassium meconate was obtained by careful treatment with dilute potassium hydroxide solution.

$$CO{<}^{CH_2 \cdot CO \cdot CO_2R}_{CH_2 \cdot CO \cdot CO_2R} \longrightarrow \left[CO{<}^{CHBr \cdot CO \cdot CO_2R}_{CH_2 \cdot CO \cdot CO_2R} \right] \longrightarrow$$

(LXXXVIII.)

$$CO{<}^{CBr:C \cdot CO_2R}_{CH=C \cdot CO_2R}{>}O \longrightarrow CO{<}^{C(OH):C \cdot CO_2K}_{CH=C \cdot CO_2K}{>}O$$
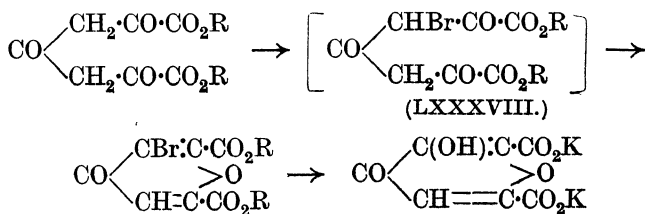
[81] F. Henrich, *Ber.*, 1921, **54**, [B], 2492; *A.*, i, 886.

[82] G. T. Morgan and H. Burgess, *T.*, 1921, **119**, 697.

[83] R. G. Fargher and H. King, *ibid.*, 292; E. Oliveri-Mandala, *Gazzetta*, 1921, **51**, i, 125; *A.*, i, 378.

[84] E. Philippi and R. Seka, *Ber.*, 1921, **54**, [B], 1089; *A.*, i, 429; compare S. Skraup and J. Priglinger, *Monatsh.*, 1910, **31**, 250; *A.*, 1910, i, 578.

[85] H. Thoms and R. Pietrulla, *Ber. deut. Pharm. Ges.*, 1921, **31**, 4; *A.*, i, 264.

The result is in itself perhaps not decisive in favour of the γ-pyrone rather than of the open-chain formula [86] for meconic acid, since it is well known that the γ-pyrone ring is easily opened.[87] In illustration of this, it has been observed that γ-pyrone reacts with aniline acetate at the ordinary temperature, yielding bishydroxymethyleneacetonedianilide (LXXXIX), from which N-phenyl-γ-pyridone (XC) is easily obtained by distillation or by treatment with acid or with sodium ethoxide.

$$CO{<}^{CH:CH}_{CH:CH}{>}O \rightarrow CO{<}^{CH:CH \cdot NHPh}_{CH:CH \cdot NHPh} \rightarrow CO{<}^{CH:CH}_{CH:CH}{>}NPh$$

(LXXXIX.)   (XC.)
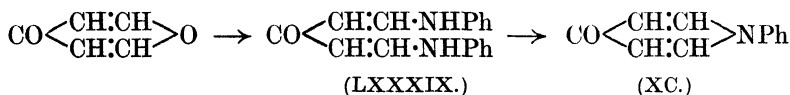
Reference may also be made to an interesting compound indirectly derived from dimethylpyrone by its hydrolysis with barium hydroxide to the barium salt of diacetylacetone. By the action of iodine on an alcoholic suspension of this salt, a compound is obtained to which the formula (XCI) is assigned, and of which the acidic properties are attributed to its existence in aqueous solution in the form (XCII) : [88]

$$CH_3 \cdot CO \cdot \overset{I}{\underset{}{CH}} \quad CH$$
$$HO \cdot C \quad CO$$
$$CH$$

(XCI.)

$$CH_3 \cdot CO \cdot \overset{H \quad OH}{\underset{}{CH}} \quad CH$$
$$HO \cdot C \quad CO$$
$$CH$$

(XCII.)
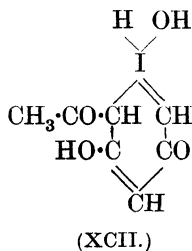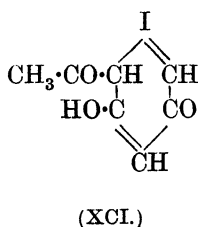
The method for the synthesis of chromones and flavones, which consists in the condensation of β-phenoxyfumaric acids by sulphuric acid and of β-phenoxycinnamoyl chlorides by aluminium chloride,[89] has been applied to the preparation of derivatives containing chlorinated benzene nuclei, and also to the preparation of 6-benzene-azoflavone :

[86] W. Borsche, *Ber.*, 1916, **49**, 2538; *A.*, 1916, i, 117; *Ann. Reports*, 1917, **13**, 131.

[87] Compare, for example, R. Willstätter and R. Pummerer, *Ber.*, 1905, **38**, 1461; *A.*, 1905, i, 457.

[88] J. N. Collie and (Miss) A. A. B. Reilly, *T.*, 1921, **119**, 1550; compare J. N. Collie and B. D. Steele, *T.*, 1900, **77**, 1116.

[89] S. Ruhemann, *Ber.*, 1913, **46**, 2188; *A.*, 1913, i, 891.
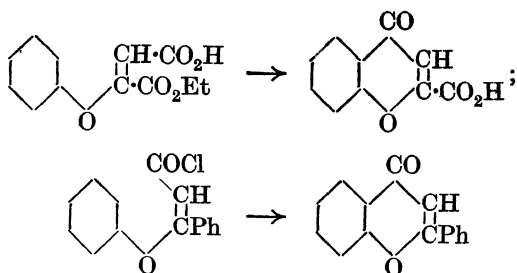
The yields of flavone derivatives are very satisfactory, but the chromones are less readily obtainable.[90] Other references to the synthesis of these compounds will be found in the section on ring formation.

2 : 2'-Dimethylchroman is formed by the direct combination of phenol with isoprene under conditions not definitely specified : [91]
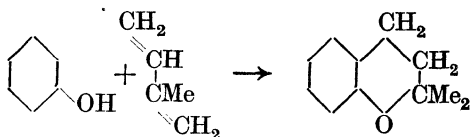
The identity of the methylated reduction product of catechin tetramethyl ether [92] is still under discussion. On the one hand,[93] it is claimed that no crystallographic difference exists between the product in question and synthetic 2 : 4 : 6 : 3' : 4'-pentamethoxy-αγ-diphenylpropane, that ordinary Gambir catechin is dextro-rotatory, acacatechin being a mixture of the lævo- with the racemic compound,[94] and hence that the reduction product about which discussion centres is also obtained from acacatechin tetramethyl ether. On the other hand,[95] the identity is claimed of acacatechin with a synthetic, and therefore inactive, 2 : 4 : 6 : 3' : 4'-penta-hydroxy-3-phenylchroman (XCIII), the tetramethyl ether of which would furnish 2 : 4 : 6 : 3' : 4'-pentamethoxy-αα-diphenylpropane on reduction. The various stages in the synthesis of the chroman are as shown :

[90] S. Ruhemann, *Ber.*, 1921, **54**, [*B*], 912; *A.*, i, 430.

[91] L. Claisen, *ibid.*, 200; *A.*, i, 263.

[92] Compare *Ann. Reports*, 1920, **17**, 110.

[93] K. Freudenberg, O. Böhme, and A. Beckendorf, *Ber.*, 1921, **54**, [*B*], 1204; *A.*, i, 576; K. Freudenberg, *Z. angew. Chem.*, 1921, **34**, 247; *A.*, i, 577.

[94] Compare also K. Feist and R. Schön, *Arch. Pharm.*, 1920, **258**, 317; *A.*, i, 47.

[95] M. Nierenstein, *T.*, 1921, **119**, 164.

$$\text{MeO} \quad \text{OMe} \atop \text{MeO} \quad \text{CH·CO·CH}_2\text{Cl} \atop \text{OMe, OMe} \rightarrow$$

$$\rightarrow$$

(XCIII.)
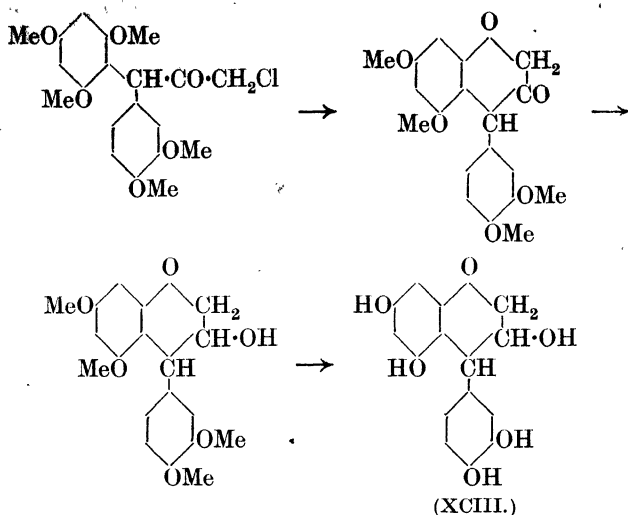
A chromone has also been identified among the products of the action of sodium on phenyl acetate.[96]   The mode of formation of 2-methylbenzo-γ-pyrone (XCIV), the compound in question, is represented by the following equations :

$$\text{CH}_3\text{·CO·O·C}_6\text{H}_5 + \text{NaOEt} \rightarrow \text{CH}_3\text{·CO}_2\text{Et} + \text{NaO·C}_6\text{H}_5$$

$$2\text{CH}_3\text{·CO·O·C}_6\text{H}_5 \rightarrow \text{H}_2 + \text{NaO·C}_6\text{H}_5 + \text{[C}_6\text{H}_4\text{]O·CO·CHNa·COMe}$$

XCIV.)
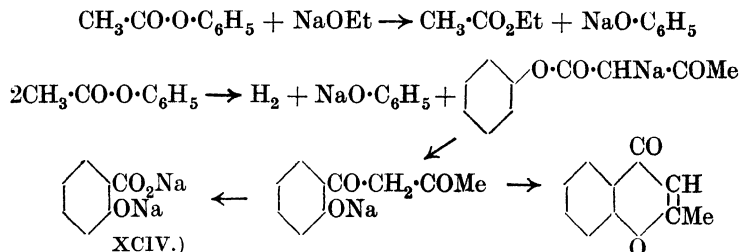
It may be noted that the production of ethyl acetate, dehydracetic acid, and salicylic acid in the course of the reaction has actually been demonstrated.   1-Hydroxy-3-methylxanthone (XCV) has also been isolated, its formation being due, it is supposed, to reactions represented as follows :

(XCV.)
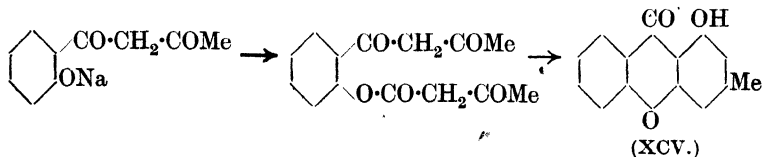
[96] W. H. Perkin, jun., *T.*, 1921, **119**, 1284.

Thiofluorescein, formed by the action of sodium sulphide on fluorescein at 110—150°, especially in presence of sodium hydroxide, has been shown to have been incorrectly designated,[97] and to have the formula (XCVI) : [98]

(XCVI.)
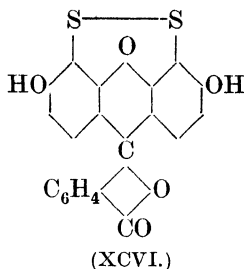
Condensation products of phenol and resorcinol with coumarin have been described, which give coloured salts and are probably analogues of phenolphthalein and fluorescein respectively.[99]

Galloflavin, one of the products of oxidation of gallic acid in alkaline solution,[1] is considered to be derived from benzo-α-pyrone.[2] It is a non-acid substance, which suffers transformation by cold potassium hydroxide solution into *iso*galloflavin.[3] Similarly, galloflavin tetramethyl ether, obtained by the aid of diazomethane,[4] is converted into *iso*galloflavin trimethyl ether. This compound, from which the tetramethyl ether may be obtained, is a lactone and also contains a carboxyl group, which is destroyed by heating the substance at its melting point, with evolution of carbon dioxide and formation of the compound (XCVII) :

$$C_{12}H_2O_4(OH)_4 \longrightarrow C_{12}H_2O_4(OMe)_4 \longrightarrow$$
Galloflavin.

$$C_{12}H_2O_4(OMe)_3(OH) \longrightarrow C_{11}H_3O_3(OMe)_3.$$
iso*Galloflavin trimethyl ether.* (XCVII.)
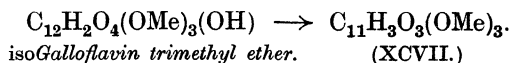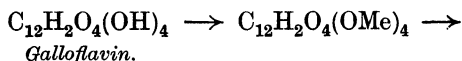
The compound (XCVII), when treated with warm potassium hydroxide with the object of opening its lactone ring, furnishes potassium formate and a salt (XCVIII), which, on acidification with hot acid, yields a new lactone (XCIX) from which potassium

[97] R. E. Meyer and J. Szanecki, *Ber.*, 1900, **33**, 2577; *A.*, 1900, i, 660.
[98] T. Maki, *J. Coll. Eng. Tokyo Imp. Univ.*, 1920, **11**, 1; *A.*, i, 183.
[99] S. Krishna, *T.*, 1921, **119**, 1420.
[1] R. Bohn and C. Graebe, *Ber.*, 1887, **20**, 2327; *A.*, 1887, 1107.
[2] J. Herzig, *Annalen*, 1920, **421**, 247; *A.*, 1920, i, 863.
[3] J. Herzig and R. Wachsler, *Monatsh.*, 1914, **35**, 77; *A.*, 1914, i, 290.
[4] J. Herzig and R. Tscherne, *ibid.*, 1904, **25**, 603; *A.*, 1904, i, 814.

acetate and $3:4:5$-trimethoxyphthalide are obtained by treatment with warm potassium hydroxide solution. From these various relationships, the formulæ (I) and (II) are deduced for galloflavin and *iso*galloflavin respectively :

(I.)

(II.)   (XCVII.)

(XCIX.)   (XCVIII.)
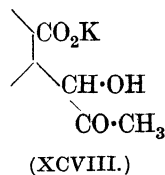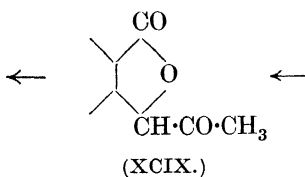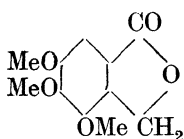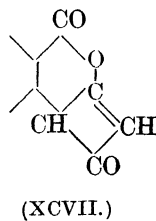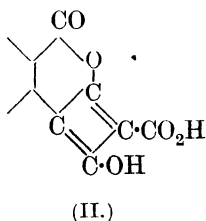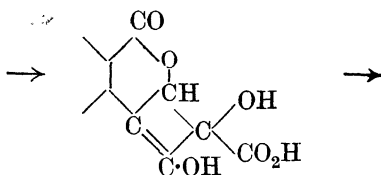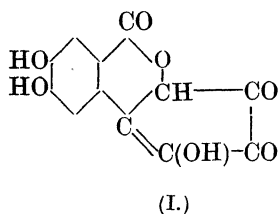
Uric Acid and its Derivatives.

Reference has already been made to the formation of $1:3$-dimethyluric acid, with other products, by direct alkylation of uric acid. This acid is conveniently accessible in the pure condition by dehydration of $1:3$-dimethyl-ψ-uric acid (III), which is produced when ψ-uric acid (IV) is treated in alkaline solution with methyl sulphate.[5] ψ-Uric acid itself is easily obtained by chlorination of uric acid in glacial acetic acid suspension at $5—10°$, and reduction in situ of the resulting 5-chloro-ψ-uric acid (V) by stannous chloride :

[5] H. Biltz and others, *Annalen*, 1921, **423**, 119; *A.*, i, 606.

$$\begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{C--NH} \\
\text{NH--C--NH} \\
\end{array}\!\!>\!\text{CO} \xleftarrow[\substack{\text{methyl} \\ \text{alcoholic} \\ \text{suspension}}]{\text{Cl}_2 +} \begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{C--NH} \\
\text{NH--C--NH} \\
\end{array}\!\!>\!\text{CO} \rightarrow \begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{C·NH·CO·NH}_2 \\
\text{NH--CO} \\
\end{array} \rightarrow$$

with OMe groups on (VII) and Cl on (V).

(VII.)   (V.)

(V) undergoes H₂O reaction downward.

$$\begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{CH·NH·CO·NH}_2 \\
\text{NH--CO} \\
\end{array}$$

(IV.)

$$\begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{C--NH} \\
\text{NH--C--NH} \\
\end{array}\!\!>\!\text{CO}$$ with OH groups

(VI.)   ← evaporation at 50° —

$$\begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{C} \\
\text{NH--CO} \\
\end{array}\!<\!\begin{array}{c}\text{OH}\\ \text{NH·CO·NH}_2\end{array}$$

$$\begin{array}{c}
\text{MeN--CO} \\
\text{CO} \quad \text{C--NH} \\
\text{MeN--C--NH} \\
\end{array}\!\!>\!\text{CO} \quad \longleftarrow \quad \begin{array}{c}
\text{MeN--CO} \\
\text{CO} \quad \text{CH·NH·CO·NH}_2 \\
\text{MeN--CO} \\
\end{array}$$

(III.)

Lack of space prevents more than reference to other items of a mass of experimental material dealing with the reactions (including alkylation) of the glycols (VI), and their ethers (VII), derived from uric acid and its alkyl derivatives by the reactions indicated.[6]

A series of papers [7] is devoted to the discussion of the products obtained from uric acid by oxidation in alkaline solution with potassium permanganate. Potassium uroxanate (VIII) will be produced if the alkaline solution be concentrated and cooled. If, however, the solution be carefully acidified with acetic acid after the addition of alcohol, potassium oxonate (or allantoxanate) (IX) will be precipitated. Allantoin (X) will, however, be obtained if the acidified solution be left to itself, or concentrated and cooled. It is concluded that the sole intermediate product is hydroxydicarbamidoethanecarboxylic acid (XI), the formation of which is the subject of an interesting discussion, which cannot be dealt with here :

$$\begin{array}{c}
\text{NH--CO} \\
\text{CO} \quad \text{C--NH} \\
\text{NH--C--NH} \\
\end{array}\!\!>\!\text{CO} \rightarrow \text{CO}\!<\!\begin{array}{c}\text{CO}_2\text{H}\\ \text{NH--C----NH}\\ \text{NH--C(OH)--NH}\end{array}\!\!>\!\text{CO} \rightarrow \text{H}_2\text{N·CO·NH·C·NH·CO·NH}_2$$

(XI.)   with CO₂H groups (VIII.)

$$\begin{array}{c}
\text{HO}_2\text{C·N:C--NH} \\
\text{CO--NH} \\
\end{array}\!\!>\!\text{CO}$$

(IX.)

$$\begin{array}{c}
\text{H}_2\text{N·CO·NH·CH·NH} \\
\text{CO--NH} \\
\end{array}\!\!>\!\text{CO}$$

(X.)

[6] H. Biltz and others, *Annalen*, 1916, **413**, 1; *A.*, 1917, i, 589.

[7] H. Biltz and R. Robl, *Ber.*, 1920, **53**, [*B*], 1950, 1964, 1967; 1921, **54**, [*B*], 2451; *A.*, 1920, i, 883, 884, 885; 1921, i, 891.

It will be noted that the original Grimeaux formula for allantoin is preferred to those more recently suggested.[8]

Reference may also be made to an investigation [9] of the various products hitherto erroneously supposed to be 5-hydroxyhydantoin. This compound is the main product of the decomposition of alloxanic acid in presence of water :

$$CO{<}{NH-C(OH)\cdot CO_2H \atop NH-CO} \longrightarrow CO_2 + CO{<}{NH-CH\cdot OH \atop NH-CO}$$

The synthesis of alkylbarbituric acids from malonic acid and the requisite carbamide may be carried out with the aid of acetic anhydride and phosphoryl chloride, whilst 5-acetyl derivatives may be obtained by the employment of an excess of acetic anhydride.[10]

The Pyridine Group.

The activity of γ-substituents in the pyridine nucleus is illustrated by a convenient synthesis of γ-alkylpyridines.[11] Chelidamic acid (XII) is easily converted by phosphorus pentachloride into 4-chloropyridine-2 : 6-dicarboxylic acid (XIII), the chlorine atom of which is more reactive than that of 4-chloropyridine itself, so that the corresponding ethyl ester reacts with ethyl sodiomalonate and its alkyl derivatives :

(XII.)   (XIII.)

The tetracarboxylic acids derived from the products by hydrolysis lose carbon dioxide on distillation. The chloro-acid has been similarly utilised for the preparation of γ-pyridyl mercaptan,[12] from which the sulphonic acid is produced by oxidation. The

[8] O. Widman, *Ber.*, 1886, **19**, 2478; L. B. Mendel and H. D. Dakin, *J. Biol. Chem.*, 1910, **7**, 153; *A.*, 1887, 30; 1910, i, 286; A: W. Titherley, *T.*, 1913, **103**, 1336.

[9] H. Biltz and (Miss) M. Kobel, *Ber.*, 1921, **54**, [*B*], 1802; *A.*, i, 815.

[10] H. Biltz and H. Wittek, *ibid.*, 1035; *A.*, i, 454.

[11] E. Koenigs and W. Jaeschke, *ibid.*, 1351; *A.*, i, 593.

[12] E. Koenigs and G. Kinner, *ibid.*, 1357; *A.*, i, 594.

direct formation of this compound by the use of sodium hydrogen sulphite appears not to have been attempted.

At a bright red heat, pyridine is decomposed, yielding mainly 2 : 2'-, with smaller quantities of 2 : 3'- and 2 : 4'-dipyridyls.[13]

N-Alkylpiperidines and piperidine nitrate will be produced in the course of a few days by the interaction of piperidine with alkyl nitrates at the ordinary temperature.[14]

The synthesis of ethyl 2 : 6-dimethylcinchomeronate from ethyl acetylpyruvate and ethyl β-aminocrotonate [15] has been shown [16] to be capable of considerable, although limited, extension by the use of analogues of each of the reactants.

Several investigations deal with the partial reduction of the pyridine nucleus. Thus, by the reduction of pyridine with zinc dust and acetic anhydride,[17] diacetotetrahydro-γγ-dipyridyl (XIV) is produced, the constitution of which is shown by its synthesis from γγ-dipyridyl (XV) by reduction with zinc dust and acetic anhydride, and by its conversion into this compound either by the action of moist air, or by oxidation with lead or manganese peroxide. This, it may be noted, is the most convenient method for preparing γγ-dipyridyl. Pyridine is the chief product of the oxidation of diacetotetrahydro-γγ-dipyridyl with a solution of iodine in potassium iodide. These results are explained by assuming the dissociation of the dipyridyl derivative in two ways :

In conformity with this view, the solution of diacetotetrahydro-dipyridyl in glacial acetic acid becomes deep blue on warming,

[13] H. Meyer and (Miss) A. Hofmann-Meyer, J. pr. Chem., 1921, [ii], 102, 287; A., i, 739.

[14] D. T. Gibson and A. K. Macbeth, T., 1921, 119, 438.

[15] Ann. Reports, 1918, 15, 101.

[16] O. Mumm and O. Böhmer, Ber., 1921, 54, [B], 726; A., i, 439.

[17] O. Dimroth and R. Heene, ibid., 2934.

but is decolorised by air, thus showing a similar behaviour to solutions of triphenylmethyl. Again, by the action of zinc dust and benzoyl chloride [18] on pyridine, benzoylpyridinium (XVI) is obtained in brown leaflets, which show the corresponding molecular weight in boiling ethylene dibromide or chlorobenzene solution, absorb oxygen from the air with consequent decolorisation, and react with halogens forming benzoic acid and $\gamma\gamma$-dipyridyl. 1-Benzylpyridinium [19] (XVII) has also been isolated in red crystals, furnishing deep blue methyl or ethyl alcoholic solutions; it is converted by halogens into 1-benzylpyridinium salts.

$$\langle \text{—} \rangle N \langle \text{CO·C}_6\text{H}_5 \qquad \langle \text{—} \rangle N \langle \text{CH}_2\text{·C}_6\text{H}_5.$$
(XVI.)   (XVII.)
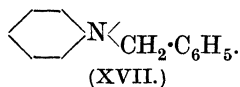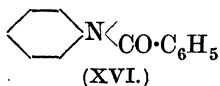
The partial reduction of certain pyridine derivatives has been accomplished by the aid of aluminium amalgam.[20] Thus ethyl collidine- and phenyl-lutidine-dicarboxylates yield the known synthetic 1 : 4-dihydro-derivatives,

$$\underset{\text{N}}{\underset{\text{Me}}{\text{EtO}_2\text{C}}} \overset{\text{R}}{\diagup} \underset{\text{Me}}{\text{CO}_2\text{Et}} \rightarrow \underset{\text{NH}}{\underset{\text{Me}}{\text{EtO}_2\text{C}}} \overset{\text{H R}}{\diagup} \underset{\text{Me}}{\text{CO}_2\text{Et}}$$
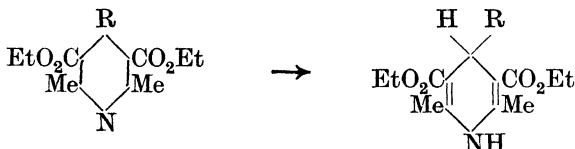
but from ethyl lutidinedicarboxylate itself, a chrome-yellow " primary " ester (XVIII) is obtained, which is reconverted into the original compound on exposure to air at the ordinary temperature, yields it with its dihydro-derivative in equimolecular proportions when heated to its melting point, and furnishes a greenish-yellow " secondary " ester (XIX) on prolonged heating below its melting point in absence of air. The secondary compound is stable in air, but suffers a similar decomposition when fused :

(XVIII.)   (XIX.)
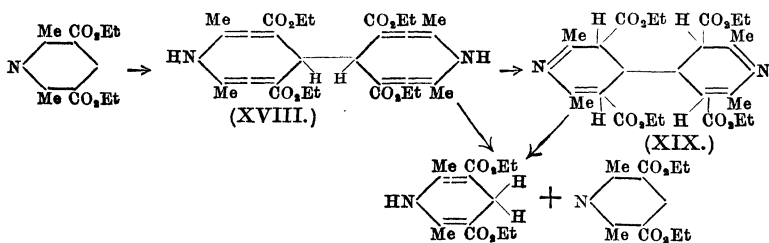
[18] E. Weitz, A. Roth, and (Miss) A. Nelken, *Annalen*, 1921, **425**, 161; *A.*, i, 804.

[19] E. Weitz, (Miss) A. Nelken (with R. Ludwig), *ibid.*, 187; *A.*, i, 804. Compare *Ann. Reports*, 1920, **17**, 106.

[20] O. Mumm and W. Beth, *Ber.*, 1921, **54**, [*B*], 1591; *A.*, i, 686.

The reader will probably find it difficult to reconcile the formula (XX) suggested for the reduction product of ethyl 2 : 6-dimethyl-cinchomeronate with the statement that it furnishes ammonia when treated with cold sodium ethoxide. By absorption of oxygen from the air, the compound in question is converted into a product, represented as (XXI), which loses water when heated, reproducing the original ester.
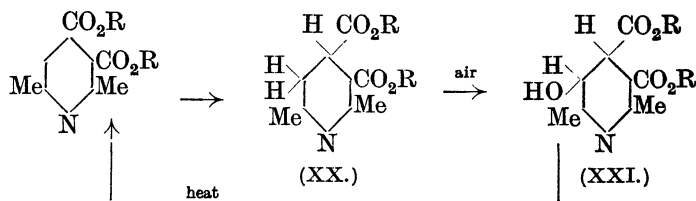
The Quinoline Group.

The yield of quinaldine is improved when the Doebner-Miller synthesis is carried out in presence of zinc chloride. At the same time, the presence of this reagent so enhances the tendency to the formation of Schiff's bases that the latter are produced in quantity sufficient to absorb the hydrogen which usually causes the production of tetrahydroquinaldine. Hence, in place of this compound, ethyl- and n-butyl-anilines are formed. The reason for the simultaneous formation of some 6-ethylquinaldine is for the time left undecided.[21]

The formation of 3-nitroquinolines by the condensation of o-aminobenzaldehyde or related compounds with methazonic acid[22] seems to be simply a particular case of Friedländer's well-known synthesis :
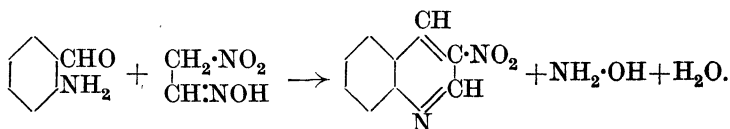
A new synthesis of 4-hydroxyquinoline-2-carboxylic (kynurenic) acid consists in the condensation of 4-methoxy-2-methylquinoline with formaldehyde, followed by oxidation of the 4-methoxy-2-quinolylethyl alcohol thus formed to 4-methoxyquinaldinic acid, and subsequent demethylation of this product : [23]

[21] W. H. Mills, J. E. G. Harris, and H. Lambourne, *T.*, 1921, **119**, 1295.

[22] W. Meister, *Ber.*, 1907, **40**, 3435; B.A.S.F., D.R.-P. 335197; *A.*, 1907, i, 885; 1921, i, 517.

[23] E. Besthorn *ibid.*, 1921, **54**, [*B*], 1330; *A.*, i, 600.

F*
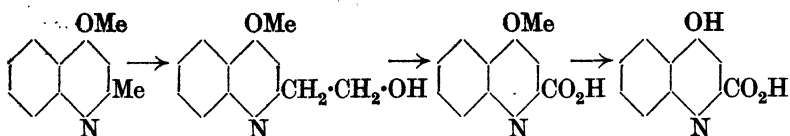
The reactivity of methyl groups in the methylquinolines is considerably greater in the 2- than in the 4-position.[24]

The conversion of benzeneazo-5-aminoquinoline into the 5-hydroxy-derivative by boiling with dilute mineral acid for a short time [25] would seem to indicate that it easily assumes the quinoneimide form :
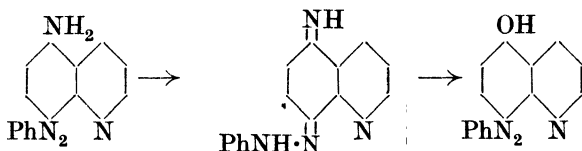
An examination [26] of the cyanines and the *iso*cyanines has supported the conclusions summarised last year,[27] and indirect confirmation of these has been supplied by syntheses of the parent ψ-*iso*cyanine, so called because its mode of formation from quinaldine corresponds with that of the *iso*cyanines from lepidine. The ψ-compound results from the action of alcoholic potassium hydroxide on a mixture of 2-iodoquinolyl methiodide and quinaldine methiodide,[28] and also by the action of methyl iodide on *N*-methyl-2-quinolylenequinaldine, the synthesis of which has been discussed on p. 117. It is hoped that an application of the latter method will permit a synthesis of *iso*cyanine. The formula for quinoline-red (XXII) seems an adequate expression of its synthesis by the action of benzal chloride on di-2-quinolylmethane.[29]

(XXII.)   (XXIII.)
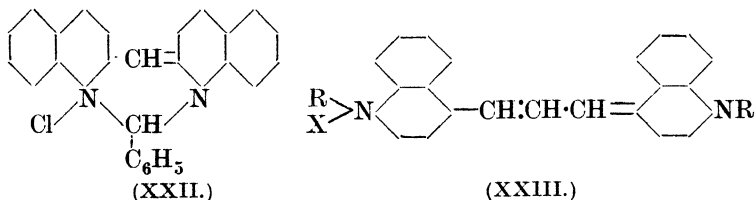
[24] O. Fischer, G. Scheibe, P. Merkel, and R. Müller, *J. pr. Chem.*, 1919, [ii], **100**, 91 ; *A.*, i, 55.

[25] W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1920, **42**, 2278 ; *A.*, i, 44.

[26] W. König and O. Treichel, *J. pr. Chem.*, 1921, [ii], **102**, 63 ; *A.*, i, 738.

[27] *Ann. Reports*, 1920, **17**, 121.

[28] O. Fischer and G. Scheibe, *J. pr. Chem.*, 1919, [ii], **100**, 86 ; *A.*, i, 56.

[29] G. Scheibe, *Ber.*, 1921, **54**, [B], 786 ; *A.*, i, 451.

(XXIV.)
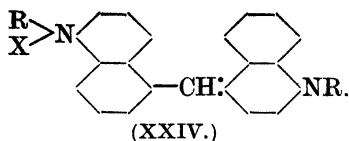
Kryptocyanines are produced by the action of alkali on hot dilute alcoholic solutions of lepidine alkyl iodides in presence of formaldehyde or chloroform.[30] Since this reaction corresponds closely with that by which pinacyanol[31] is produced from quinaldine ethiodide, it will probably be found that the new dyes have the formula (XXIII), rather than (XXIV) tentatively suggested by their discoverers.

Alkaloids.

Further progress has been made towards the synthesis of quinine and its derivatives along the lines indicated in last year's Report.[32] Homonicotinic acid, obtained by the oxidation of lepidine, has been converted into β-collidine by the reactions indicated : [33]
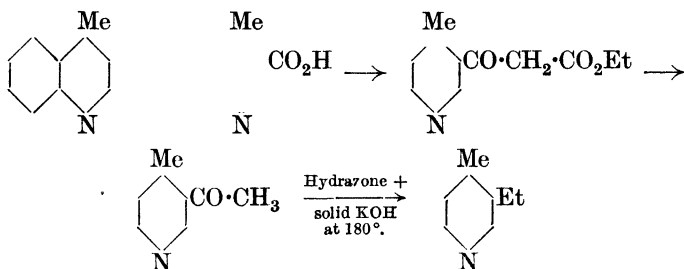
The method previously successfully applied to the synthesis of β-4-piperidylpropionic acid has been extended to the conversion of β-collidine into homocincholeupone,[34] and protection has been obtained for the process whereby the latter compound is utilised for the preparation of dihydro-cinchoninone and -quininone.[35] A general method[36] for the reduction of 4-quinolyl ketones by zinc or aluminium powder and sodium ethoxide has the advantage that it leaves unchanged the unsaturated side-chain in, for example, quininone. Its application to dihydrocinchoninone results in the

[30] E. A. Adams and H. L. Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661 ; *A.*, i, 129.

[31] Compare *Ann. Reports*, 1920, **17**, 122. [32] P. 117.

[33] P. Rabe and E. Jantzen, *Ber.*, 1921, **54**, [*B*], 925 ; *A.*, i, 438.

[34] E. Koenigs and W. Ottmann, *ibid.*, 1343 ; *A.*, i, 595.

[35] Ver. Chinin-Fabr. Zimmer & Co., D.R.-P. 330945 ; *A.*, i, 360 ; compare *Ann. Reports*, 1920, **17**, 118.

[36] *Idem*, D.R.-P. 330813 ; *A.*, i, 355.

formation of the four possible isomerides, of which the relationship may be represented by the following symbols :

$$
\begin{array}{cccc}
H-C-N< & H-C-N< & >N-C-H & >N-C-H \\
H-C-OH & HO-C-H & H-C-OH & HO-C-H
\end{array}
$$
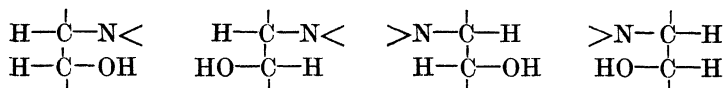
Of these, two correspond with the minor cinchona alkaloids; the remaining two, which were previously unknown, may be reconverted by known methods through dihydrocinchotoxine into the original dihydrocinchoninone.

Space does not permit of more than passing reference to the interesting results of the action of bromine on dihydroquinine and dihydrocupreine,[37] and of diazotising 5-aminocinchona alkaloids.[38]

Previous syntheses of compounds closely related to quinine have been supplemented by those of the compounds (XXV) and (XXVI).[39] Thus, 1-methyl-2-pyridone was converted by catalytic reduction into the lactam of δ-methylaminovaleric acid (XXVII). It was not previously known that such lactams are amenable to the Claisen condensation. In the present case, the compound (XXVIII) was synthesised by this means, and treated successively with bromine and sodium hydroxide :
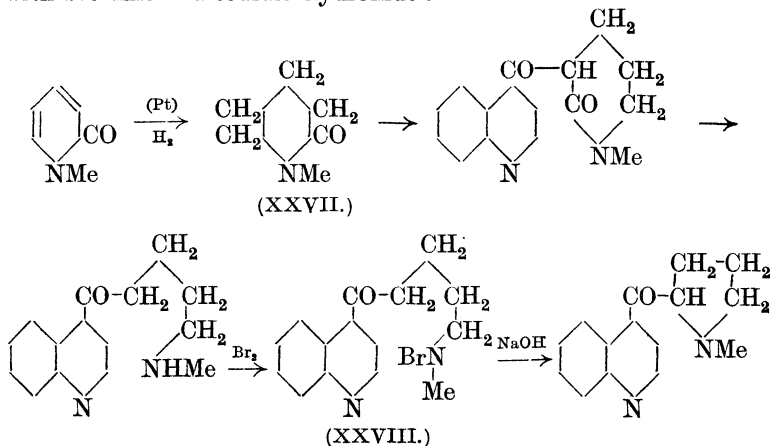
(XXVII.)

(XXVIII.)

In a similar manner, a homologue of (XXVIII) is obtained from ε-methylaminohexoic lactam,

$$
\begin{array}{c}
CH_2-CH_2-CH_2 \\
CH_2-CH_2-CO
\end{array}\!\!>\!\!NMe .
$$
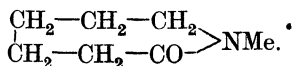
[37] R. Weller, *Ber.*, 1921, **54**, [B], 230; *A.*, i, 265.

[38] G. Giemsa and J. Halberkann, *ibid.*, 1167; *A.*, i, 581.

[39] L. Ruzicka and C. T. Seidel, *Helv. Chim. Acta*, 1921, **4**, 472; *A.*, i, 585.

The suggestion that harmine is a methylmethoxy-4-carboline [40] (XXIX) is now confirmed [41] by its degradation to norharman (4-carboline) (XXX) by two separate methods, and the synthesis of the latter compound. 1-Methylindole-2-carboxylic acid (XXXI) is converted through its chloride into 1-methylindole-2-carboxy-acetalylamide (XXXII), which, when treated with alcoholic hydrochloric acid, furnishes 5-keto-4 : 5-dihydroindolediazine (XXXIII), from which norharman is obtained by distillation with zinc dust :
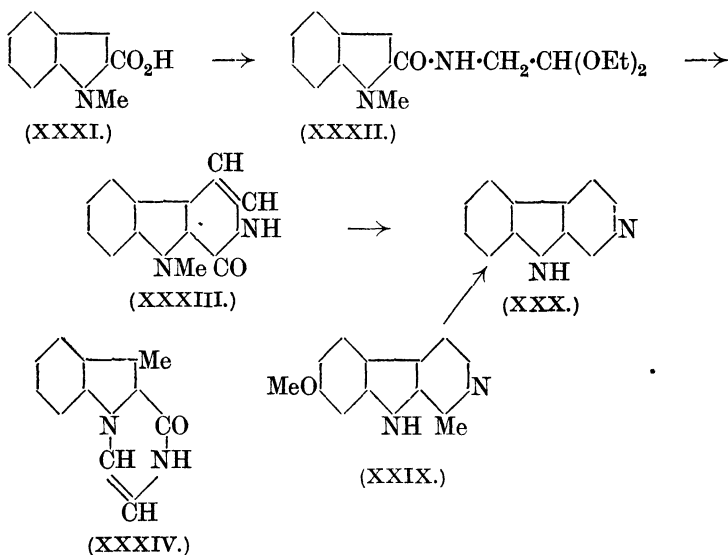
A synthesis of norharmine on similar lines is foreshadowed. The necessity for using N-methylindole derivatives arises from the fact that the unmethylated compound gives rise to 5-keto-7-methyl-4 : 5-dihydroindolediazine(1 : 4) (XXXIV). Norharman also results from the condensation of tryptophan with formaldehyde in presence of sulphuric acid, followed by oxidation of the product :
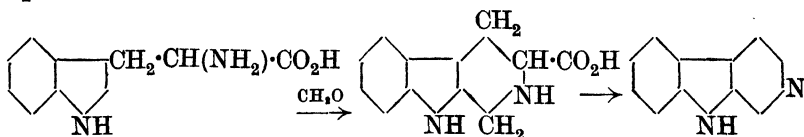
Since harman (with which the alkaloids aribine,[42] loturine, and,

[40] Compare *Ann. Reports*, 1919, **16**, 122.
[41] W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *T.*, 1921, **119**, 1602.
[42] E. Spāth, *Monatsh.*, 1919, **40**, 351; *A.*, 1920, **i**, 327.

possibly, colloturine [43] have been identified) is obtained in a similar manner by the use of acetaldehyde, the position of the methyl group in this and in harmine is determined.

Evodiamine (XXXV) is broken down by boiling alcoholic potassium hydroxide into N-methylanthranilic acid and a base. This is considered to be 3 : 4-dihydro-5-carboline (XXXVI),
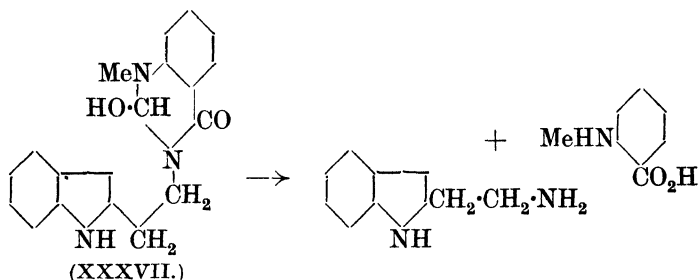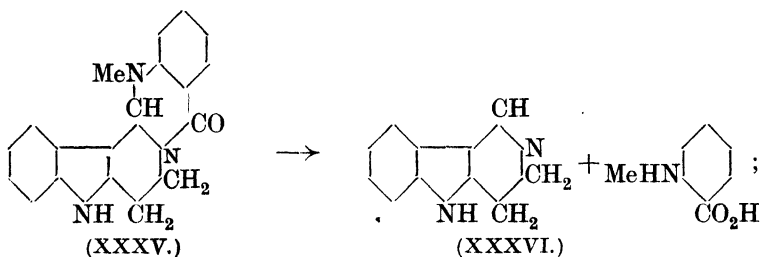
because " *iso*evodiamine " (XXXVII) (obtained from evodiamine by boiling with two per cent. alcoholic hydrochloric acid) is similarly decomposed into N-methylanthranilic acid and a base, thought to be 2-β-aminoethylindole, since it yields 2-indolecarb-oxylic acid on fusion with potassium hydroxide.[44] It has been pointed out,[45] however, that the last piece of evidence is incon-clusive, since the same acid is one of the products of the alkaline fusion of scatole(3-methylindole), and, further, that it is improb-able that derivatives of 5- as well as of 4-carboline should occur naturally.

Laurotetanine is a phenolic secondary base, which readily oxidises. It is converted by " nascent " diazomethane into its methyl ether, but by preformed diazomethane into N-methyl-laurotetanine methyl ether, which is designated *iso*glaucine owing

[43] E. Späth, *Monatsh.*, 1920, **41**, 297; *A.*, i, 50.
[44] Y. Asahina and S. Mayeda, *J. Pharm. Soc. Japan*, 1916, No. 416; *A.*, i, 48.
[45] W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *loc. cit.*

to its isomerism with, and similarity to, glaucine (XXXVIII).[46] For this reason, and in view of the oxidation of laurotetanine to 1 : 2-dimethoxybenzene-3 : 4 : 5-tricarboxylic acid, the formula (XXXIX) is assigned to *iso*glaucine : [47]

(XXXVIII.)   (XXXIX.)
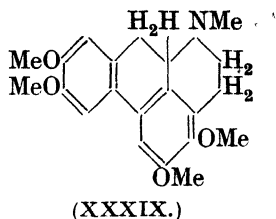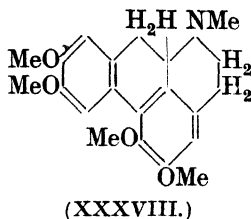
A more detailed account of the synthesis of ecgonine outlined in last year's Report has since been published.[48]

A reinvestigation [49] of the degradation of scopoline by exhaustive methylation has shown that it proceeds normally under very low pressure if silver be excluded from solution. The product is not however, uniform, since a mixture of four dihydrodemethylscopolines is obtained by reducing it. One of these, a crystalline compound, is unchanged by treatment with sodium methoxide, whilst from the oily mixture of the remaining three a product (XLIII) is obtained corresponding with O-methyl-*iso*-ψ-demethylscopoline. This is attributed to the presence in the original mixture of the compound (XLII), corresponding in structure with ψ-demethylscopoline :

(XLI.)   (XL.)

(XLII.)   (XLIII.)
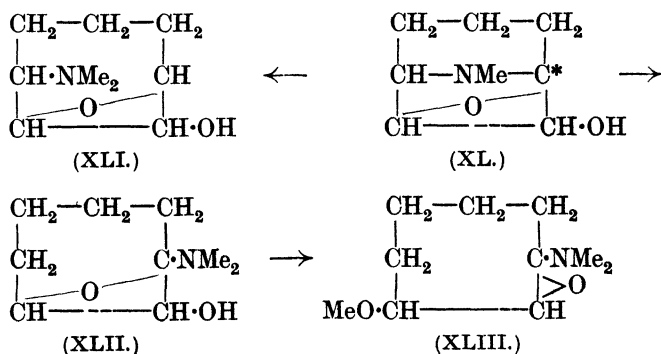
Against the formula (XL) for scopoline it has been urged that

[46] Compare J. Gadamer, *Arch. Pharm.*, 1911, **249**, 680; *A.*, 1912, i, 48.

[47] K. Gorter, *Bull. Jard. bot. Buitenzorg*, 1921, [iii], **3**, 180; *A.*, i, 587.

[48] R. Willstätter and M. Bommer, *Annalen*, 1921, **422**, 15; *A.*, i, 122.

[49] K. Hess, *Z. angew. Chem.*, 1921, **34**, 393; *A.*, i, 683.

when the oxygen bridge of *l*-scopoline is broken down by treatment with hydrobromic acid, the resulting product is inactive, although the asterisked carbon atom would retain its asymmetry. For this reason, formula (XLIV) is put forward.[50]   This argument, however, loses much of its force from the fact that the same experimenter found that cold chlorosulphonic acid also ruptures the bridge linking, and the hydroxyscopoline obtained by subsequent hydrolysis is lævorotatory.

(XLIV.)   (XLV.)
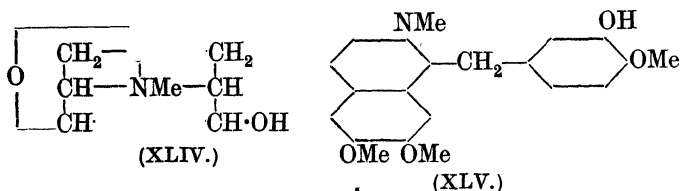
It has hitherto been a matter of uncertainty as to which of the four methoxyl groups in laudanosine is represented by a hydroxyl group in laudanine. Since, however, ethyl- and ethylcarbonato-laudanines are respectively oxidised to 3-ethoxy- and 3-ethylcarbonato-4-methoxybenzoic acids, it follows that the formula of laudanine is represented by the formula (XLV).[51]

The view that palmatine, one of the Colombo alkaloids, only differs from berberine (XLVI) in that it contains two methoxy-groups in place of the methylenedioxy-grouping [52] has been confirmed synthetically.[53]   By treatment of tetrahydroberberine with methyl-alcoholic potassium hydroxide at 180°, its two methoxy- and its methylenedioxy-groups were converted into four hydroxyl groups. The tetramethoxy-derivative prepared from this product by the aid of methyl sulphate was identical with tetrahydropalmatine, and was converted into palmatine itself by oxidation with alcoholic iodine solution. A methyltetrahydropalmatine (XLVII) has also been prepared from palmatine by the action of magnesium methyl iodide, followed by reduction of the resulting α-methyl-dihydropalmatine.[54]   The product is not identical with corydaline, so that this alkaloid cannot have the constitution (XLVII) previously assigned to it.[55]

[50] J. Gadamer, *Arch. Pharm.*, 1921, **259**, 110; *A.*, i, 588.
[51] E. Späth, *Monatsh.*, 1920, **41**, 297; *A.*, i, 50.
[52] K. Feist and G. Sandstede, *Arch. Pharm.*, 1918, **256**, 1.
[53] E. Späth and N. Lang, *Ber.*, 1921, **54**, [B], 3064.   •
[54] *Idem, ibid.*, 3074; *A.*, 1922, i, 166.
[55] J. J. Dobbie and A. Lauder, *P.*, 1902, **17**, 252; J. Gadamer, *Arch. Pharm.*, 1916, **254**, 295; *A.*, 1917, i, 472; H. Legerholtz, *ibid.*, 1918, **256**, 729.

(XLVI.) (XLVII.)
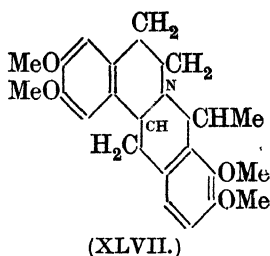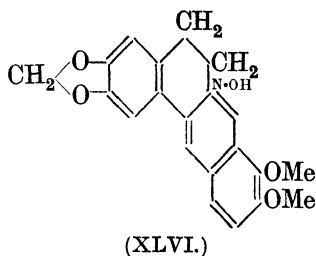
By the action of sulphoacetic acid on papaverine, the sulphoacetate of a new base, coralyne, is obtained. This compound is so named owing to its close relationship to the synthetic coralydine, into the α-form of which it has been converted by reduction.[56]

Passing reference may be made to a discussion of the mutual relationships of the *iso*quinoline alkaloids.[57] Ethyl chloroformate promises to be a useful reagent for the investigation of these compounds, since it has been found to break down the tetrahydro-*iso*quinoline ring, but to have little effect on the dihydroindole, pyrrolidine, piperidine, and tetrahydroquinoline rings.[58] For example, bulbocapnine (XLVIII) is converted into ethyl bulbo-capninecarboxylate (XLIX) :

(XLVIII.) (XLIX.)
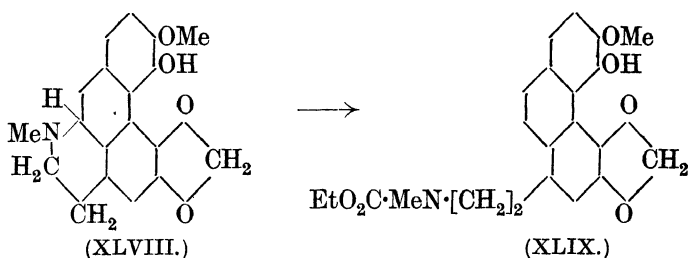
In the morphine group, attention is being concentrated on a study of the various reduction products obtainable from thebaine and codeine, and their derivatives.[59]

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[56] W. Schneider and K. Schroeter, *Ber.*, 1920, **53**, [*B*], 1459; *A.*, i, 760; W. Schneider and A. Köhler, *ibid.*, 1921, **54**, [*B*], 2031; *A.*, i, 803.

[57] J. W. D. Hackh, *Chem. News*, 1921, **123**, 178; *A.*, i, 800.

[58] J. Gadamer and F. Knoch, *Arch. Pharm.*, 1921, **259**, 135; *A.*, i, 579.

[59] C. Mannich and (Miss) H. Löwenheim, *ibid.*, 1920, **258**, 295; M. Freund and E. Speyer, *Ber.*, 1920, **53**, [*B*], 225; A. Skita, *ibid.*, 1921, **54**, [*B*], 1560; E. Speyer and S. Siebert, *ibid.*, 1519; E. Speyer and others, D.R.-P. 338147; *A.*, i, 124, 125, 684, 685, 803.

ANALYTICAL CHEMISTRY.

THE analytical work published during the past year has been greater in volume and more diverse in character than in any other year since the outbreak of the war. Hence, in order to confine a general survey within the space available, it has been necessary to make a selection from the more important contributions, and to omit many which would otherwise have received notice.

Physical Methods.

The influence of adsorption on the accuracy of analytical results has been demonstrated in a series of papers. For example, filter-paper adsorbs a considerable proportion of lead, and smaller amounts of copper and silver. The main cause of this is the mineral matter in the paper, and the presence of an acid solution (that is, hydrogen ions) prevents the adsorption.[1] The amount of acid adsorbed by filter-paper is equivalent to the alkalinity of the ash.[2] The amounts of alkali taken up are directly proportional to the alkalinity of the solution, but in this case there is no true adsorption.[3] The removal of heavy metals by cellulose is due to a chemical reaction, and is not a physical process.[4] The use of impure asbestos leads to error owing to the adsorption of positive ions. Advantage may be taken of this fact for the estimation of lead in water.[5] The absorption of salts of metals or of alkaloids by glass-wool appears to be due to the alkalinity of the glass, and the loss may be considerable if this material is used for the filtration of hot solutions.[6] Reference may also be made, in this connexion, to the influence of the glass of certain bottles of recent manufacture on standard acid and other solutions.[7]

Several new methods of analysis have been based on the determination of the temperature of miscibility of two or more liquids. For example, the alcoholic strength of aqueous alcohol may be rapidly ascertained by mixing the liquid with acetone or light

[1] I. M. Kolthoff, *Pharm. Weekblad*, 1920, **57**, 1510; *A.*, ii, 19.
[2] *Idem, ibid.*, 1571; *A.*, ii, 123.
[3] *Idem, ibid.*, 1921, **58**, 46; *A.*, ii, 213.   [4] *Idem, ibid.*, 233; *A.*, ii, 277.
[5] *Idem, ibid.*, 401; *A.*, ii, 344.   [6] *Idem, ibid.*, 463; *A.*, ii, 409.
[7] C. A. Mitchell, *Analyst*, 1921, **46**, 129.

petroleum,[8] and in the case of ternary mixtures, such as alcohol, ether, and water, the composition may be found from the quantity of water required to produce turbidity, or of ether to obtain a clear liquid.[9] Similarly, the critical temperature of solution in aniline of light petroleum, before and after nitration, affords a measure of the hydrocarbons present.[10] The lowering of the temperature at which a mixture of hydrocarbons and aniline separates into two layers, after sulphonation, corresponds directly with the proportion of aromatic hydrocarbons in the mixture.[11]

The use of nephelometric methods has been extended in several directions, and a new type of nephelometer has been constructed, in which the height of a standard Tyndall cone is measured in the liquid under examination and in a standard solution. In all such measurements, it is essential that the particles of the turbid liquid should be of uniform size.[12] For certain biochemical estimations, the turbidimeter of Folin and Denis [13] is preferable to the nephelometer.[14]

An addition to the numerous applications of refractometry in analytical work has been published, the principle having been adapted to the calculation of the proportions of salts in an aqueous solution.[15]

For the spectroscopic examination of mixtures, the use of the X-ray spectrum has the advantage of relative simplicity as compared with the ordinary spectrum. A vacuum spectrograph has been devised, by means of which photographs of the lines of all the elements may be readily obtained.[16]

There have not been many contributions to the methods of determining viscosity, but reference may be made to the cup-and-ball viscosimeter, in which the time before a ball falls from an inverted cup in which a drop of the oil has been placed is measured. This gives results comparable with those obtained with standard apparatus.[17]

[8] H. Rosset, *Ann. Chim. anal.*, 1921, [ii], **3**, 235; *A.*, ii, 598.

[9] L. Desvergnes, *Mon. Sci.*, 1921, **11**, 145; *A.*, ii, 601.

[10] G. Chavanne and L. J. Simon, *Ann. Chim. anal.*, 1921, [ii], **3**, 87; *A.*, ii, 354.

[11] H. T. Tizard and A. G. Marshall, *J. Soc. Chem. Ind.*, 1921, **40**, 20T; *A.*, ii, 280.

[12] H. Kleinmann, *Kolloid Z.*, 1920, **27**, 236; *A.*, ii, 56.

[13] O. Folin and W. Denis, *J. Biol. Chem.*, 1914, **18**, 263; *A.*, 1914, ii, 687.

[14] W. Denis, *ibid.*, 1921, **47**, 27; *A.*, ii, 555.

[15] C. A. Clemens, *J. Ind. Eng. Chem.*, 1921, **13**, 813; *A.*, ii, 650.

[16] M. Siegbahn, A. E. Lindh, and N. Stensson, *Z. Physik*, 1921, **4**, 61; *A.*, ii, 344.

[17] T. C. Thomsen, *Report of Lubrication Inquiry Committee, Dept. Scientific and Ind. Research,* 1920, **15—16,** 103.

A new instrument for determining the surface tension of liquids from the rise in capillary tubes has been devised, and is intended especially for cases where only a small amount of the liquid is available.[18]

Gas Analysis.

Several new forms of apparatus for use in gas analysis have been designed. One of these is an absorption vessel the stopper of which is hollow and has a perforated extension reaching nearly to the bottom of the flask, and the gas is made to pass through this stopper on its way through the absorbent.[19] Another apparatus is a gas-volume compensator, by means of which the volume of a constituent absorbed from a gas may be obtained with an accuracy of within 0·5 per cent. from the reading shown on a manometer.[20]

A new method for the estimation of microscopically small quantities of gas has been based on the consecutive determination of the condensation temperature of each gas when cooled in the side tube of a Pirani gauge. In practice, the results are compared with those obtained with a series of gauges each containing a pure gas, and the respective amounts are found by reference to graphs.[21]

The methods principally used for the estimation of small quantities of carbon monoxide in air are those based on its oxidation by means of iodic anhydride,[22] and on its conversion into carboxyhæmoglobin.[23] Elimination of the influence of other gases reacting with iodic anhydride is not always easy; for this reason, the second method is often preferable, but air containing more than 0·1 per cent. of carbon monoxide must be diluted before being passed through the hæmoglobin solution.[24]

A reagent termed " Hoolamite " (U.S. Pats. 1321061—2) consists of a mixture of iodic anhydride, fuming sulphuric acid, and pumice stone. The carbon dioxide formed in the oxidation of the carbon monoxide reacts with the excess of sulphur trioxide to form a green compound, and the intensity of the coloration, when compared with special colour standards, affords a measure of the carbon monoxide. The method is applicable to gases containing up to 0·2 per cent. of carbon monoxide.[25]

[18] S. Sugden, T., 1921, 119, 1483.

[19] Walz, Chem. Ztg., 1921, 45, 658; A., ii, 515.

[20] R. S. Tour, Chem. Met. Eng., 1920, 23, 1104; A., ii, 125.

[21] Research Staff, Gen. Electric Co., Ltd. (W. R. Campbell), Proc. Physical Soc., 1921, 33, 287; A., ii, 591.

[22] A. Gautier, Compt. rend., 1898, 126, 793; A., 1898, ii, 537.

[23] J. Ogier and E. Kohn-Abrest, Ann. Chim. anal., 1908, 13, 169; A., 1908, ii, 631.

[24] D. Florentin and H. Vandenberghe, Compt. rend., 1921, 172, 391; A., ii, 276.

[25] C. R. Hoover, J. Ind. Eng. Chem., 1921, 13, 770; A., ii, 654.

Two modifications of the Pettenkofer method of estimating carbon dioxide in air have been devised, the gas in each case being absorbed by standard sodium hydroxide solution, the excess of which is subsequently titrated.[26]

A gravimetric method of estimating nitrous fumes in air, etc., has been based on the formation of an orange precipitate when a solution of a nitrite is heated at 50° first with a solution of p-nitroaniline and then with an alkaline solution of α-naphthol.[27]

The fact that iodine converts metals such as silver, copper, or aluminium into iodides at the ordinary temperature has been utilised for the detection of chlorine in air. When a sheet of silver forming part of an electric circuit is covered with damp potassium iodide any chlorine present in the air will liberate iodine, which will then combine with the metal, and break the electric circuit; this may be notified audibly by the addition of a suitable device.[28]

It has been shown that adsorption of small quantities of benzene hydrocarbons in coal gas by means of charcoal, and their subsequent distillation with steam, give more accurate results than are obtainable by the dinitrobenzene or paraffin methods.[29]

Agricultural Analysis.

Various methods for the estimation of colloidal material in soil have been published. One of these, depending on a physical separation of " ultra clay " by centrifugal action, gave results in agreement with those calculated from the absorption of dry ammonia by the soil.[30]

Considerable attention has also been directed to the estimation of hydrogen-ion concentration as an indication of the lime requirement of soils. A convenient colorimetric method has been devised, and in using this for estimating the lime requirement increasing quantities of barium hydroxide are added to the soil, prior to the extraction, a curve plotted of the successive hydrogen-ion concentrations, and the amounts of barium hydroxide calculated into calcium oxide.[31]

The method of estimating soil acidity by the liberation of iodine from a solution of potassium iodide and iodate [32] has been shown to be influenced by too many factors to be really trustworthy.[33]

[26] J. Freund, *Z. Hyg.*, 1920, **91**, 218; *A.*, ii, 348.

[27] J. Moir, *J. S. African Assoc. Anal. Chem.*, 1921, **4**, 3; *A.*, ii, 345.

[28] C. Matignon, *Compt. rend.*, 1921, **172**, 532; *A.*, ii, 272.

[29] E. Berl, K. Andress, and W. Müller, *Z. angew. Chem.*, 1921, **34**, 125; *A.*, ii, 272.

[30] C. J. Moore, W. H. Fry, and H. E. Middleton, *J. Ind. Eng. Chem.*, 1921, **13**, 527; *A.*, ii, 608.

[31] E. A. Fisher, *J. Agric. Sci.*, 1921, **11**, 45; *A.*, ii, 349.

[32] A. Stutzer and W. Haupt, *J. Landw.*, 1915, **63**, 33; *A.*, 1915, ii, 655.

[33] O. Lemmermann and L. Fresenius, *ibid.*, 1921, **69**, 97; *A.*, ii, 516.

A new method of estimating potassium in soils, even in the presence of considerable amounts of sodium salts, depends on its precipitation as cobaltinitrite, and measurement of the volume of the precipitate.[34] The method of Folin and Macallum[35] does not give accurate results unless the soil is suspended in a saturated salt solution.[34]

A rapid test for readily-soluble phosphates in soils is based on the extraction of the air-dried sample with standard nitric acid, precipitation of the phosphate with ammonium molybdate at 60°, and measurement of the amount of the precipitate.[36]

Apparently the presence of other salts in the soil retards the precipitation of the magnesium ammonium phosphate in the estimation of citric-soluble phosphate, and the liquid should therefore be left over-night before filtration.[37]

A micro-Kjeldahl method, which enables nitrogen to be estimated in a few mg. of material, has been described; methyl-red is used as the indicator in the titration.[38]

For the estimation of ammoniacal nitrogen in fertilisers containing calcium cyanamide and ammonium salts, the solution is treated with sodium hydroxide and a current of air aspirated through it into standard acid for about seven hours at the ordinary temperature.[39]

A direct method of estimating dicyanodiamide in mixed fertilisers depends on its precipitation with silver picrate, which does not give a precipitate with cyanamide or carbamide.[40] An analogous method has been based on the precipitation of a compound of 2 mols. of dicyanodiamide with 1 mol. of silver picrate, whilst carbamide and dicyanodiamidine are not precipitated. Dicyanodiamide also forms similar silver complexes with soluble nitrophenols, such as the silver salt of trinitroresorcinol, which gives even more accurate results than silver picrate.[41]

The principle may also be used as the basis of a volumetric process, the excess of silver remaining after the precipitation of the complex silver picrate dicyanoguanidine being titrated.[42]

[34] O. Arrhenius, *Medd. K. Vctenskapakad., Nobel-Inst.*, 1920, **4**, 1; *A.*, ii, 412.

[35] O. Folin and A. B. Macallum, *J. Biol. Chem.*, 1912, **11**, 523; *A.*, 1912, ii, 683.

[36] O. M. Shedd, *Soil Sci.*, 1921, **11**, 111; *A.*, ii, 274.

[37] P. Müller, *Chem. Ztg.*, 1921, **45**, 178; *A.*, ii, 275.

[38] W. Geilmann, *J. Landw.*, 1920, **68**, 235; *A.*, ii, 128.

[39] J. Froidevaux and H. Vandenberghe, *Ann. Chim. ànal.*, 1921, **3**, 146; *A.*, ii, 462.

[40] R. N. Harger, *J. Ind. Eng. Chem.*, 1920, **12**, 1107; *A.*, ii, 224.

[41] E. B. Johnson, *J. Soc. Chem. Ind.*, 1921, **40**, 125; *A.*, ii, 468.

[42] *Idem, J. Ind. Eng. Chem.*, 1921, **13**, 533; *A.*, ii, 605.

Carbamide in fertilisers may be accurately estimated by pre-cipitation as carbamide oxalate, which is then purified, dried under reduced pressure, and weighed.[42]

Organic Analysis.

Qualitative.—Some new sensitive colour reactions with alkaline phenylhydrazine hydrochloride solution containing metal or diazo-benzenesulphonic acid have been devised for the identification of formaldehyde and acetaldehyde.[43] Resorcinol with sulphuric acid is also a very sensitive reagent for formaldehyde after separation in a current of steam.[44] In this way, the test may be used in the presence of tartaric and oxalic acids, which also give colorations with the reagent.[45]

Further work has been done on the identification of organic acids by conversion into their phenacyl esters, which are then separated by fractional crystallisation.[46]

Lactic acid gives a characteristic red coloration with alcoholic guaiacol solution, and may thus be distinguished from formic, acetic, malic, benzoic, salicylic, and certain other acids.[47]

A method for the detection of free tartaric acid in wines has been based on its partial extraction with amyl alcohol, in which potassium hydrogen tartrate and calcium tartrate are insoluble.[48]

The biochemical process of detecting dextrose [49] has been found a suitable means for the examination of plant material.[50] A reagent giving a brown coloration with woody fibre and with vanillin consists of a solution of vanadium pentoxide in phosphoric acid solution; it may be used as a microscopic test.[51]

Phenol may be identified by giving a characteristic, coloured zone when mixed with sodium nitrite solution and poured on to the surface of sulphuric acid.[52]

A test capable of detecting 1 part of fluorescein in 200,000,000 parts consists in acidifying the solution with sulphuric or hydro-chloric acid, shaking it with ether, and, after separation of the

[42] E. B. Johnson, *J. Ind. Eng. Chem.*, 1921, **13**, 533; *A.*, ii, 605.

[43] E. Pittarelli, *Arch. Farm. Sperim. Sci. Aff.*, 1920, **30**, 148; *A.*, ii, 222.

[44] R. Cohn, *Chem. Ztg.*, 1921, **45**, 997; *A.*, ii, 663.

[45] E. Krausz and H. Tampke, *ibid.*, 521; *A.*, ii, 466.

[46] J. B. Rather and E. E. Reid, *J. Amer. Chem. Soc.*, 1921, **43**, 629; *A.*, ii, 356. Compare *A.*, 1920, i, 381.

[47] E. Hartwig and R. Saar, *Chem. Ztg.*, 1921, **45**, 322; *A.*, ii, 356.

[48] L. Mathieu, *Ann. Falsif.*, 1921, **14**, 281; *A.*, ii, 662.

[49] Compare *Ann. Reports*, 1920, **17**, 138.

[50] M. Bridel and R. Arnold, *Compt. rend.*, 1920, **172**, 1434; *A.*, ii, 465.

[51] J. Grüss, *Ber. Deut. bot. Ges.*, 1921, **38**, 361; *A.*, ii, 284.

[52] G. Rodillon, *J. Pharm. Chim.*, 1921, [vii], **23**, 136; *A.*, ii, 282.

ethereal layer, adding a few drops of ammonia, when a green coloration is produced when fluorescein is present.[53]

The green coloration produced by concentrated sulphuric acid with certain lactic and cinnamic acid derivatives is due to the formation of indones, which combine with the sulphuric acid, whereas hydrindones do not give the reaction. It is possible in this way to distinguish between stable cinnamic acids and *allo*-compounds.[54]

Methods of distinguishing between volatile alkylamines and ammonia, and between volatile tertiary and primary or secondary alkylamines have been based on their respective behaviour with formaldehyde, and with potassium mercuric iodide.[55]

Glycine anhydride, creatinine, and some allied compounds give a coloration when heated with picric acid; this reaction, however, is also given by numerous other substances.[56]

It has been shown the thalleioquinine reaction is most sensitive when the proportion of bromine is as 6 atoms per molecule of quinine; it is capable of detecting 1 part of the alkaloid in 250,000 parts.[57]

Theobromine may be distinguished from caffeine by the differences in the colorations produced when the respective bismutho-iodides are reduced by means of hydriodic acid.[58]

Hitherto no definite colour reaction of aconite has been known, but it has recently been shown that aconitine, or at all events ψ-aconitine, the alkaloid in Indian aconite, gives a distinctive green coloration with potassium ferricyanide and formic acid.[59]

A new method of distinguishing between ouabain and strophantin is based on the difference in the behaviour of the two glucosides when warmed with hydrochloric acid and resorcinol. Strophantin gives a rose coloration, whilst ouabain gives no coloration, this difference being due to the action of the respective sugars formed in the hydrolysis.[60]

No distinctive test for vitamins has yet been discovered, but it has been found that some constituent of antiscorbutic extracts, possibly a polyphenol readily detached from a vitamin, gives a blue coloration with a sulphuric acid solution of sodium tungstate,

[53] M. Lombard, *Bull. Soc. chim.*, 1921, [iv], **29**, 462; *A.*, ii, 528.

[54] R. de Fazi, *Gazzetta*, 1921, **51**, i, 164; *A.*, ii, 357.

[55] H. E. Woodward and C. L. Alsberg, *J. Biol. Chem.*, 1921, **46**, 1; *A.*, ii, 358.

[56] T. Sasaki, *Biochem. Z.*, 1921, **114**, 63; *A.*, ii, 358.

[57] W. B. Hart, *J. Soc. Chem. Ind.*, 1921, **40**, 72T; *A.*, ii, 359.

[58] M. Malmy, *J. Pharm. Chim.*, 1921, [vii], **23**, 89; *A.*, ii, 360.

[59] S. Mallaneh, *Analyst*, 1921, **46**, 193; *A.*, ii, 470.

[60] A. Richaud, *J. Pharm. Chim.*, 1921, **24**, 161; *A.*, ii, 601.

phosphomolybdic acid, and phosphoric acid. Extracts which do not possess antiscorbutic properties do not give this coloration, which, however, is also produced by quinol.[61]

Quantitative.—Two new types of combustion furnace have been designed, one of which has many advantages over the ordinary furnace,[62] whilst the other is a compact micro-furnace, which can also be used for the estimation of nitrogen.[63]

A new method for the estimation of enols has been based on the fact that they form complex copper salts which are soluble in chloroform,[64] but it has been shown that the method is only applicable to a very limited number of cases.[65]

Simple volatile alcohols may be estimated by esterification with lauryl chloride, extraction of the ester with ether, and its hydrolysis with potassium hydroxide, but the method is not satisfactory with secondary alcohols of the type of menthol.[66]

A rapid method of estimating ethyl alcohol is to add aniline and to titrate the liquid with water until a permanent turbidity results, the volume of alcohol being then found by reference to a graph.[67]

For the estimation of ethyl acetoacetate advantage has been taken of the fact that the ester reacts with sodium sulphite, with the liberation of sodium hydroxide, which is subsequently titrated.[68]

It has been shown that the accuracy of the iodometric method of estimating acetone depends mainly on the proportion of potassium hydroxide added to the solution.[69]

A new method of estimating glycerol in wines depends on its conversion into acraldehyde by means of boric acid, and estimation of the distilled aldehyde by means of standard silver nitrate solution.[70]

There have been but few additions to the methods of analysing oils and fats, but it has been shown that propyl alcohol is a useful medium for obtaining complete substitution in the determination of the bromine-substitution value.[71] A simple and trustworthy formula for calculating the acetyl value from the saponification

[61] N. Bezssonoff, *Compt. rend.*, 1921, **173**, 466; *A.*, ii, 608.
[62] T. J. Hedley, *T.*, 1921, **119**, 1242.
[63] W. Dautwitz, *Chem. Ztg.*, 1920, **44**, 963; *A.*, ii, 131.
[64] W. Hieber, *Ber.*, 1921, **54**, [B], 902; *A.*, ii, 466.
[65] W. Dieckmann, *ibid.*, 2251; *A.*, ii, 716.
[66] A. Grün and T. Wirth, *Z. Deut. Oel-Fett Ind.*, 1921, **41**, 145; *A.*, ii, 660.
[67] A. Lachman, *J. Ind. Eng. Chem.*, 1921, **13**, 230; *A.*, ii, 355.
[68] H. Yanagisawa, *J. Pharm. Soc. Japan*, 1921, 240; *A.*, ii, 418.
[69] P. H. Hermans, *Chem. Weekblad*, 1921, **18**, 348; *A.*, ii, 467.
[70] A. Heiduschka and F. Englert, *Z. anal. Chem.*, 1921, **60**, 161; *A.*, ii, 524.
[71] E. Schulek, *Pharm. Zentr.-h.*, 1921, **62**, 391; *A.*, ii, 603.

values of a fat before and after acetylation has been worked out,[72] and a more exact method of separating solid from liquid fatty acids in the form of their lead salts has been devised.[73]

The conditions under which cholesterol and allied substances may be accurately estimated have been studied, and the colorimetric method has been shown to be inapplicable to the unsaponifiable matter of fæces.[74]

A new measure for the activity of amylase solutions has been recommended as giving more absolute values—$Sf = K \times$ maltose (in grams)/enzyme preparation (grams), where K represents the constant of the unimolecular reaction during the first part of the hydrolysis.[75]

In using taka diastase for the estimation of starch, the results vary with the origin of the enzymic preparation, and it is therefore necessary to make control experiments on pure starch with each enzyme.[76]

An iodometric method of estimating the diastatic capacity of malt has been based on the oxidation of the resulting maltose to maltobionic acid by means of an alkaline solution of iodine, the amount of iodine required affording a measure of the maltose.[77]

The conditions under which dextrose is quantitatively oxidised by alkaline permanganate have also been ascertained and adapted to the estimation of starch and dextrose,[78] and the same principle has also been used for the estimation of lactose.[79]

Lævulose, like other sugars and polyhydric alcohols, combines with boric acid to form an acid compound, and the proportion of boric acid entering into combination affords a means of estimating that sugar.[80]

A new volumetric method of estimating reducing sugars involves the use of an alkaline solution of potassium ferricyanide standardised against pure dextrose.[81]   The process may be used for the estimation of dextrose formed in the hydrolysis of certain glucosides.[82]

[72] E. André, *Compt. rend.*, 1921, 172, 984; *A.*, ii, 419.

[73] E. Twitchell, *J. Ind. Eng. Chem.*, 1921, 13, 806; *A.*, ii, 662.

[74] J. A. Gardner and M. Williams, *Biochem. J.*, 1921, 15, 363, 376; *A.*, ii, 563.

[75] H. von Euler and O. Svanberg, *Z. physiol. Chem.*, 1921, 112, 193; *A.*, ii, 528.

[76] E. Horton, *J. Agric. Sci.*, 1921, 11, 240; *A.*, ii, 661.

[77] J. L. Baker and H. F. E. Hulton, *Analyst*, 1921, 46, 90; *A.*, ii, 420.

[78] F. A. Quisumbing, *Philippine J. Sci.*, 1920, 16, 581; *A.*, ii, 67.

[79] F. T. Adriano, *ibid.*, 1920, 17, 213; *A.*, ii, 284.

[80] G. van B. Gilmour, *Analyst*, 1921, 46, 3; *A.*, ii, 221.

[81] A. Jonescu and V. Vargolici, *Bul. Soc. Chim. Románia*, 1920, 2, 38; *A.*, ii, 283.   [82] A. Jonescu, *ibid.*, 1921, 3, 6; *A.*, ii, 525.

A colorimetric method of estimating dextrose in urine has been based on the fact that when heated in the presence of sodium carbonate it reduces 4 : 6-dinitroguaiacol to 4-nitro-6-aminoguaiacol, which has an intense colour.[83]

Another suitable reagent for the colorimetric estimation of dextrose is 3 : 5-dinitrosalicylic acid.[84]

An iodometric method of estimating phenylhydrazine has been devised, and adapted to the estimation of pentosans and pentoses.[85]

Lævulic acid in foods may be estimated by oxidation with dichromate and sulphuric acid, and distillation and titration of the resulting acetic acid. Formic, acetic, and lactic acids must first be separated from the original substance.[86]

For the separation of aliphatic amines, advantage has been taken of the solubility of ammonium chloride and monomethylamine hydrochloride in chloroform. The ammonia may then be separated by treatment with yellow mercuric oxide, whilst trimethylamine may be separated from dimethylamine by converting it into its periodide.[87]

An accurate method of titrating aniline involves diazotisation with standard sodium nitrite solution, potassium iodide-starch paper being used as outside indicator.[88]

Better results are obtained in the titration of certain alkaloids by using bromophenol-blue in place of the usual indicators, whilst methyl-red is the most suitable indicator for quinine hydrogen salts.[89]

Theobromine can be separated in a very pure condition by means of a method in which tetrachloroethane is used for the extraction.[90]

Inorganic Analysis.

Qualitative.—The applications of spot reactions on filter-paper as a preliminary test have been systematised, and attention has been directed to the use of the reactions of aluminium, uranium, and chromium with alizarin colouring matters and of manganese with benzidine.[91]

It has been shown that sodium thioantimonate is a useful general

[83] J. B. Sumner, *Physiol. Abstr.*, 1921, **6**, 170; *A.*, ii, 526.

[84] J. B. Sumner and V. A. Graham, *J. Biol. Chem.*, 1921, **47**, 5; *A.*, ii, 564.

[85] A. R. Ling and R. D. Nanji, *Biochem. J.*, 1921, **15**, 466; *A.*, ii, 601.

[86] L. Grünhut, *Z. Unters. Nahr. Genussm.*, 1921, **41**, 261; *A.*, ii, 602.

[87] H. Franzen and A. Schneider, *Biochem. Z.*, 1921, **116**, 195; *A.*, ii, 663.

[88] T. Sabalitscka and H. Schrader, *Z. anal. Chem.*, 1921, **34**, 45; *A.*, ii, 224.

[89] N. Evers, *Pharm. J.*, 1921, **106**, 470; *A.*, ii, 527.

[90] R. V. Wadsworth, *Analyst*, 1921, **46**, 32; *A.*, ii, 225.

[91] F. Feigl and R. Stern, *Z. anal. Chem.*, 1921, **60**, 1; *A.*, ii, 279.

reagent for certain metals. In the case of mercury, the colour of the precipitate varies with the particular salt.[92]

A delicate test for the hydrides of arsenic, antimony, and phosphorus has been based on the fact that they produce a violet coloration on sodium aurochloride test-paper.[93]

As little as 0·00000034 gram of gaseous ammonia may be detected by the film-mirror which it produces on a drop of silver nitrate solution containing 3 per cent. of formaldehyde.[94] Another new test for ammonia depends on its conversion into hexamethylenetetramine picrate, which forms characteristic, microscopic crystals.[95]

Several tests for individual metals will be found useful in systematic analysis. A reaction capable of detecting mercury in a solution of 2 mg. per litre depends on the formation of cuprous mercuric iodide; it is applied in the form of test-paper.[96]

Bettendorff's reagent (stannous chloride in hydrochloric acid) is capable of detecting 0·01 mg. of arsenic trioxide; in the case of dark solutions, the arsenic is first evolved as hydrogen arsenide.[97]

A method of detecting antimony in the presence of tin is based on its precipitation from hydrochloric acid solution as red oxysulphide by means of sodium thiosulphate solution, whereas stannic chloride gives a white precipitate of sulphide and hydroxide. Cupric salts must be removed before applying the test.[98]

Aluminium, iron, chromium, and manganese may be detected by the form and colour of their crystalline compounds with salicylic acid.[99]

A new and sensitive reagent for the detection of cobalt is either a nitroso-compound or an oxamino-compound, which is prepared by heating an acidified solution of R-salt (sodium β-naphthol-3 : 6-disulphonate) with sodium nitrite. Its aqueous solution forms a green compound with ferrous salts, a brownish-yellow compound with nickel, and a deep red dye with cobalt.[1] Iron and cobalt may also be distinguished from nickel by the colorations given by their salts with dimethylglyoxime solution and ammonia.[2]

Comparative tests of the sensitiveness of the ordinary reagents for barium ion have shown that sulphuric and chromic acids are

[92] A. Langhans, Z. anal. Chem., 1921, **60**, 91; A., ii, 353.

[93] W. Zimmermann, Apoth. Ztg., 1921, **36**, 29; A., ii, 276.

[94] C. D. Zenghilis, Compt. rend., 1921, **173**, 153; A., ii, 558.

[95] C. Collo and V. Teodossiu, Bul. Soc. Chim. România, 1920, **2**, 100; A., ii, 214.

[96] P. Artmann, Z. anal. Chem., 1921, **60**, 81; A., ii, 350.

[97] L. W. Winkler, Pharm. Zentr.-h., 1921, **62**, 125; A., ii, 275.

[98] V. Njegovan, Chem. Ztg., 1921, **45**, 681; A., ii, 563.

[99] C. van Zijp, Pharm. Weekblad, 1921, **58**, 694; A., ii, 463.
H. S. van Klooster, J. Amer. Chem. Soc., 1921, **43**, 746; A., ii, 415.

[2] W. Vaubel, Z. öffentl. Chem., 1921, **27**, 163; A., ii, 596.

the most sensitive (1 : 1,600,000 and 1 : 1,200,000) and sodium arsenate the least sensitive (1 : 175).[3]

A simple method of detecting sodium and potassium in the presence of magnesium depends on the formation of the compound $K_2CuPb(NO_3)_6$, which crystallises in microscopic, black cubes, and of sodium pyroantimonate, which also has a characteristic microscopic appearance.[4]

The reaction between azoimide and nitrous acid—$HNO_3 + HN_3 = H_2O + N_2O + N_2$—has been applied to the detection of nitric acid in the presence of nitrous acid, the latter being thus removed before testing for the former.[5]

In applying the diphenylamine test, it is necessary to have a definite concentration of the liquid, and this is best found by adding successive quantities of water.[6]

Quantitative.—Guanidine carbonate, being non-hygroscopic, is a convenient substance to use for the standardisation of acid solutions.[7] Another original standard, which gives trustworthy results in alkalimetry, is potassium hydrogen oxalate.[8]

Two new forms of apparatus for colorimetric estimations have been devised.[9]

In using cresol-red as indicator in determinations of hydrogen-ion concentration a correction is necessary for the presence of salt.[10] Some indicators are too sensitive for certain estimations, such as the titration of an alkali acetate with an acid; in such cases, tropæolin-O and -OO may be serviceable.[11] By using two indicators simultaneously it is possible to titrate many coloured solutions with accuracy,[12] and in some cases, where this method is not applicable, the colouring matter may be bleached with hydrogen peroxide.[13]

When only small amounts of solution are available, indicator papers may be used in presence of a buffer solution.[14]

The new indicators described include a compound prepared by

[3] O. Lutz, *Z. anal. Chem.*, 1921, **60**, 209; *A.*, ii, 596.

[4] E. Ludwig and (Mlle) H. Spirescu, *Bul. Soc. Chim. Románia*, 1920, **2**, 78; *A.*, ii, 215.

[5] E. Oliveri-Mandalà, *Gazzetta*, 1921, **51**, i, 138; *A.*, ii, 346.

[6] A. E. Weinhagen, *J. Amer. Chem. Soc.*, 1921, **43**, 685; *A.*, ii, 346.

[7] A. H. Dodd, *J. Soc. Chem. Ind.*, 1921, **40**, 89T; *A.*, ii, 409.

[8] Y. Osaka and K. Andô, *J. Tokyo Chem. Soc.*, 1920, **41**, 945; *A.*, ii, 132.

[9] E. Alstone, *Soil Sci.*, 1920, **10**, 467; *A.*, ii, 214. N. Evers, *Analyst*, 1921, **46**, 392; *A.*, ii, 705.

[10] R. C. Wells, *J. Amer. Chem. Soc.*, 1920, **42**, 2160; *A.*, ii, 55.

[11] I. M. Kolthoff, *Z. anorg. Chem.*, 1921, **115**, 168; *A.*, ii, 465.

[12] J. L. Lizius, *Analyst*, 1921, **46**, 355; *A.*, ii, 650.

[13] C. A. Mitchell, *ibid.*, 131.

[14] I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 961; *A.*, ii, 515.

the interaction of ethyl nitrate and magnesium phenyl bromide,[15] and two new phthaleins, one of which is unaffected by excess of alkali or alcohol; both are available between P_H 8·9 and 10·2.[16]

There have been but few additions to the general methods of oxidation or reduction. It has been shown, however, that the addition of manganese sulphate accelerates the reaction between potassium permanganate and hydrogen peroxide or sodium oxalate.[17]

A sharp method of titrating arsenious compounds with standard dichromate solution is to add potassium bromide and hydrochloric acid, and to pass a current of air through the liquid. The bromine liberated by the first drop in excess of dichromate is carried over into potassium iodide solution and the liberated iodine indicated by means of starch.[18] An analogous method may be used for the titration of ferrous salts with permanganate solution.[19]

An oxidimetric method of estimating manganese in hydrofluoric acid solution by means of potassium permanganate has been shown to give results as accurate as those obtained by other volumetric processes.[20]

A volumetric method of estimating mixtures of permanganate, dichromate, and chromic salts is based on the fact that permanganate is converted into hydrated manganese dioxide by the action of manganese sulphate and zinc sulphate, whilst dichromate is unaffected. By titrating the liquid with ferrous sulphate solution before and after this treatment, the amounts of the two substances are found.[21]

For the estimation of traces of hydrogen peroxide, ferrous sulphate is used as the reducing agent, and the resulting ferric sulphate estimated colorimetrically.[22]

Mention may also be made of a volumetric method of estimating hyposulphite depending on its reducing action on potassium ferricyanide.[23]

The use of cadmium has been recommended in place of zinc for the reduction of ferric salts, since it obviates the risk of iron being deposited when insufficient iron is present.[24] Quadrivalent titanium is also quantitatively reduced by cadmium, and it is therefore

[15] R. W. Kinkead, *Chem. News*, 1921, **122**, 4; *A.*, ii, 124.

[16] W. Csánzi, *Z. Elektrochem.*, 1921, **27**, 64; *A.*, ii, 270.

[17] P. H. Segnitz, *J. Ind. Eng. Chem.*, 1920, **12**, 1196; *A.*, ii, 125.

[18] R. Meurice, *Ann. Chim. anal.*, 1921, **3**, 85; *A.*, ii, 85.

[19] R. Meurice, *ibid.*, 23; *A.*, ii, 218.

[20] J. Holluta and J. Obrist, *Monatsh.*, 1921, **41**, 555; *A.*, ii, 522.

[21] N. G. Chatterji, *Chem. News*, 1921, **123**, 232; *A.*, ii, 713.

[22] F. W. Horst, *Chem. Ztg.*, 1921, **45**, 572; *A.*, ii, 461.

[23] R. Formhals, *ibid.*, 1920, **44**, 869; *A.*, ii, 58.

[24] W. D. Treadwell, *Helv. Chim. Acta*, 1921, **4**, 551; *A.*, ii, 523.

possible to estimate iron and titanium simultaneously by first reducing the solution, and then titrating it with permanganate.[25]

Several new iodometric methods have been published during the year. When titrating an excess of iodine in acid solution with thiosulphate solution, a sharper end-point may be obtained by adding thiosulphate so as to prevent the ionic concentration of the iodine.[26]

Lead may be accurately estimated as chromate by iodometric estimation of the excess of chromate in the filtrate from the lead chromate.[27] For the iodometric estimation of iron it is essential to have definite concentrations of acid and potassium iodide, and a limit for the proportion of iron.[28]

An iodometric method of estimating chromium in chromite [29] has been devised; and new methods of estimating iodides in the presence of iodates,[30] and thiosulphates in the presence of sulphites and tetrathionates,[31] also involve iodometric processes.

Turning next to the methods of separating metals, we find an important investigation of the conditions under which zinc, cadmium, manganese, and silver may be estimated by volatilising their sulphides in a current of dry hydrogen sulphide.[32]

The use of hypophosphorous acid in gravimetric analysis has also been studied, and methods have been devised for its use in separating silver from platinum and other metals.[33]

Mercuric chloride can be completely volatilised from its solution in a current of hydrogen chloride, and the principle has been adapted to the separation of mercury from copper, cadmium, iron, and other elements.[34]

Two new volumetric methods of estimating mercury have also been described.[35]

Gravimetric methods for the estimation of cadmium have been based on its precipitation as sulphide containing sulphate ion,[36]

[25] W. D. Treadwell and A. Rheiner, *loc. cit.*

[26] B. Kohler, *Chem. Listy*, 1920, **14**, 137, 195; *A.*, ii, 410.

[27] C. W. Simmons, J. R. Gordon, and H. C. Boehmer, *Canad. Chem. J.*, 1920, **4**, 139; *A.*, ii, 63.

[28] I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 1510; *A.*, ii, 713.

[29] E. Little and J. Costa, *J. Ind. Eng. Chem.*, 1921, **13**, 228; *A.*, ii, 351.

[30] V. Thüringer, *Bul. Soc. Chim. România*, 1920, **2**, 73; *A.*, ii, 214.

[31] A. Kurtenacker and A. Fritsch, *Z. anorg. Chem.*, 1921, **117**, 262; *A.*, ii, 556.

[32] L. Moser and A. Schattner, *Chem. Ztg.*, 1921, **45**, 758; *A.*, ii, 558.

[33] L. Moser and T. Kittl, *Z. anal. Chem.*, 1921, **60**, 145; *A.*, ii, 521.

[34] W. Strecker and K. Conradt, *Ber.*, 1920, **53**, [*B*], 2113; *A.*, ii, 64.

[35] E. Biilmann and K. Thaulow, *Bull. Soc. chim.*, 1921, [iv], **29**, 587; *A.*, ii, 560.

[36] L. W. Winkler, *Chem. Ztg.*, 1921, **34**, 383; *A.*, ii, 539.

and on its precipitation as cadmium ammonium phosphate.[37] Bismuth may also be accurately estimated as phosphate.[38]

Small quantities of arsenic may be estimated colorimetrically by comparing the stain produced by arsenic hydride on mercuric chloride paper, with those produced by known amounts of arsenic. The advantage claimed for the method over the Gutzeit process is that the stains are permanent.[39]

Antimony may be separated from tin by precipitation as sulphide from a strong hydrochloric acid solution at 80°, the tin sulphide remaining in solution at 25°. The addition of ammonium chloride lowers the temperature of precipitation, and the best results are obtained with a definite concentration of hydrochloric acid.[40]

Zinc may be estimated gravimetrically by precipitation as ammonium zinc phosphate,[41] whilst a volumetric method is to precipitate the metal by means of the double thiocyanate of mercury and potassium, and to titrate the filtrate with mercuric nitrate, iron alum being used as indicator.[42]

In the absence of certain metals, such as copper and zinc, nickel may be estimated in the presence of cobalt by titration with potassium cyanide solution.[43]

Nickel and cobalt may be separated by simultaneous precipitation as xanthates, and treatment of the precipitate with dilute nitric acid,[44] which dissolves only the nickel compound.

Cobalt gives a brown coloration with dimethylglyoxime in the presence of mineral acids, and a colorimetric method of estimation has been based on this fact.[45]

A method of separating ferric, aluminium, and chromium hydroxides is to boil the precipitate with 10 per cent. sodium hydroxide solution containing sodium perborate, which dissolves the aluminium and chromium hydroxides.[46]

A new process of estimating iron and manganese depends on

[37] L. W. Winkler, Z. angew. Chem., 1921, **34**, 466; A., ii, 656.

[38] W. R. Schoeller and E. F. Waterhouse, Analyst, 1920, **45**, 435; A., ii, 135.

[39] J. Cribier, J. Pharm. Chim., 1921, [vii], 24; A., ii, 653.

[40] G. Luff, Chem. Ztg., 1921, **45**, 229, 254, 274, 291; A., ii, 353.

[41] L. W. Winkler, Z. angew. Chem., 1921, **34**, 235; A., ii, 521.

[42] I. M. Kolthoff and C. van Dijk, Pharm. Weekblad, 1921, **58**, 538; A., ii, 413.

[43] G. H. Stanley, J. S. African Anal. Chem., 1921, **4**, 10; A., ii, 351.

[44] A. Whitby and J. P. Beardwood, J. Chem. Met. Soc. S. Africa, 1921, **21**, 199; A., ii, 562.

[45] S. A. Bradley and F. B. Hobart, J. Amer. Chem. Soc., 1921, **43**, 482; A., ii, 351.

[46] (Mme) M. and M. Lemarchands, Ann. Chim. anal., 1921, **3**, 86; A., ii, 351.

their precipitation as hydroxides by means of hexamethylene-tetramine.[47]

A method of estimating gallium, in the absence of zinc, is to precipitate it as ferrocyanide, to decompose the precipitate with hydrogen peroxide or sodium hydroxide, and to precipitate the gallium as hydroxide.[48]

Investigation of the methods of separating aluminium from glucinum has shown that accurate results are obtainable by precipitating the metals as hydroxides, dissolving the precipitate in the smallest possible amount of sodium hydroxide solution, and boiling the solution to precipitate the glucinum hydroxide.[49]

Under specified conditions, separation by means of sodium hydrogen carbonate [50] also gives satisfactory results.[51]

Colorimetric methods of estimating small amounts of chromium in steel have been published, one of these being based on the red coloration given by chromic acid with diphenylsemicarbazide solution.[52]

For the estimation of vanadium in steels and iron alloys precipitation with " cupferron " (the ammonium salt of nitrosophenyl-hydroxylamine) gives trustworthy results.[53] The reagent is also applicable to the separation of zinc from uranium.[54]

A hydrolytic process of separating some of the rare earths by means of creams of insoluble oxides and carbonates has been developed.[55]

It has been shown that the composition of potassium platini-chloride as usually separated does not correspond with the formula K_2PtCl_6, but that results much closer to the theoretical value may be obtained by precipitating the salt with alcohol, and drying the salt at 110°.[56]

A new method of estimating potassium in silicates by precipitation as perchlorate is available in the absence of sodium and calcium sulphates.[57] For the estimation of potassium in the presence of sodium and magnesium sulphates and phosphates

[47] C. Kollo, *Bul. Soc. Chim. Románia*, 1920, **2**, 89; *A.*, ii, 218.

[48] L. E. Porter and P. E. Browning, *J. Amer. Chem. Soc.*, 1921, **43**, 111; *A.*, ii, 277.

[49] H. T. S. Britton, *Analyst*, 1921, **46**, 359; *A.*, ii, 657.

[50] C. L. Parsons and S. K. Barnes, *J. Amer. Chem. Soc.*, 1906, **28**, 1589; *A.*, 1907, ii, 52.

[51] H. T. S. Britton, *Analyst*, 1921, **46**, 437; *A.*, ii, 712.

[52] B. S. Evans, *ibid.*, 285; *A.*, ii, 562.

[53] L. Rolla and M. Nuti, *Giorn. Chem. Ind. Appl.*, 1921, **3**, 287; *A.*, ii, 597.

[54] A. Angeletti, *Gazzetta*, 1921, **51**, i, 285; *A.*, ii, 524.

[55] A. C. Neish and J. W. Burns, *Can. Chem. Met.*, 1921, **5**, 69; *A.*, ii, 560.

[56] A. Vürtheim, *Chem. Weekblad*, 1920, **17**, 637; *A.*, ii, 61.

[57] J. J. Morgan, *J. Ind. Eng. Chem.*, 1921, **13**, 225; *A.*, ii, 349.

advantage has been taken of the fact that potassium perchlorate is insoluble in methyl alcohol, whilst sodium and magnesium perchlorates, phosphates, and sulphates are soluble.[58]

Another new method depends on the precipitation of potassium as picrate.[59]

A colorimetric method of estimating traces of bromine has been based on the coloration which it gives with Schiff's reagent.[60]

A new reagent termed " fornitral " (formic acid in combination with *endo*-anilodiphenyldihydrotriazole) gives a quantitative precipitate with nitric acid.[61]

Hypochlorites may be rapidly estimated by a gasometric method, which consists in treating them with an alkaline solution of hydrazine and measuring the nitrogen evolved.[62]

Strychnine forms an insoluble phosphomolybdate, and advantage has been taken of the fact for the estimation of small quantities of phosphoric acid.[63] Another method has been based on the formation of a dense yellow liquid, immiscible with water, when phosphoric acid is shaken with ether in the presence of another acid and an alkali molybdate. This yellow liquid is separated by centrifuging and its volume read.[64]

The difference in the solubility of the respective silver salts in 0·5 to 1·5N-sodium hydroxide solution affords a means of separating arsenates and arsenites.[65]

Electrochemical Analysis.

A simple apparatus, which can be made in the laboratory, has been devised for the electrometric determination of hydrogen-ion concentration.[66] Another apparatus has for its aim the measurement of hydrogen-ion concentration without allowing any volatile matter to escape.[67]

The principles applicable to conductivity titrations have been elucidated, and it has been shown that in the case of very weak acids and bases accurate results are obtained only within definite limits for the concentration and dissociation constants. Methods

[58] H. Atkinson, *Analyst*, 1921, **46**, 354; *A.*, ii, 654.

[59] St. Minovici and A. Jonescu, *Bul. Soc. Chim. România*, 1921, **3**, 25; *A.*, ii, 520.

[60] F. Oppenheimer, *Arch. Exp. Path. Pharm.*, 1921, **89**, 17; *A.*, ii, 273.

[61] *Ann. Chim. anal.*, 1921, [ii], **3**, 207; *A.*, ii, 558.

[62] A. Macbeth, *Chem. News*, 1921, **122**, 268; *A.*, ii, 461.

[63] G. Embden, *Z. physiol. Chem.*, 1921, **113**, 138; *A.*, ii, 462.

[64] H. Copaux, *Compt. rend.*, 1921, **173**, 656; *A.*, ii, 707.

[65] G. W. Sears, *J. Amer. Chem. Soc.*, 1921, **43**, 466; *A.*, ii, 347.

[66] G. W. Monier-Williams, *Analyst*, 1921, **46**, 315; *A.*, ii, 650.

[67] A. B. Hastings, *J. Biol. Chem.*, 1921, **46**, 463; *A.*, ii, 460.

for reducing the dissociation of salts, and for correcting the results where the dissociation limits have been exceeded, have therefore been devised.[68]

The catalytic production of formic acid when the solution in a hydrogen electrode contains carbonates is a probable source of error in electrometric estimations with such electrodes.[69]

The low results obtained in the electrolytic deposition of mercury have been investigated, and the conditions for accurate estimation determined. When the cyanide method is used, it is essential that the current should not be too strong, and that a large amount of potassium cyanide should not be present.[70]

When a silver cathode is used for the electro-deposition of copper, the deposit may be readily removed by means of an ammoniacal solution of ammonium trichloroacetate. This dissolves copper, cadmium, and zinc readily, and nickel slightly, but does not dissolve silver.[71]

The conditions under which copper can be electrolytically estimated in solutions also containing arsenic, antimony, bismuth, selenium, and molybdenum have been investigated. As a rule, deposition of the metals only begins after the bulk of the copper has separated, but selenium and tellurium are deposited at the beginning of the electrolysis. Various reagents must therefore be employed.[72]

For the separation of mercury and copper in the presence of chlorine ions, the solution is electrolysed at a voltage of 2·2 and a relatively low amperage, and after deposition of the mercury the voltage and amperage are increased.[73]

A modified method for the electrolytic separation of copper, antimony, and tin has also been devised.[74]

For the rapid separation of gold from copper, palladium, and platinum advantage has been taken of the fact that it is quantitatively deposited from a solution of its chloride containing acetate.[75]

Vanadium, tungsten, molybdenum, ferrous salts, chromates, and tartrates interfere with the electrolytic estimation of cobalt and nickel in cobalt steels, and a method for the removal of these substances has been worked out.[76]

[68] I. M. Kolthoff, *Chem. Weekblad*, 1920, **17**, 694; *A.*, ii, 124.

[69] C. L. Evans, *J. Physiol.*, 1920, **54**, 353; *A.*, ii, 271.

[70] W. Böttger, *Z. Elektrochem.*, 1920, **26**, 445; *A.*, ii, 65.

[71] H. Waters, *J. Amer. Chem. Soc.*, 1921, **43**, 700; *A.*, ii, 414.

[72] F. G. Hawley, *Eng. and Min. J.*, 1920, **110**, 162; *A.*, ii, 216.

[73] W. Böttger, *Z. angew. Chem.*, 1921, **34**, 120; *A.*, ii, 351.

[74] F. Foerster and D. Aanensen, *Z. Elektrochem.*, 1921, **27**, 10; *A.*, ii, 350.

[75] W. D. Treadwell, *Helv. Chim. Acta*, 1921, **4**, 364; *A.*, ii, 416.

[76] G. E. F. Lundell and J. F. Hoffmann, *J. Ind. Eng. Chem.*, 1921, **13**, 540; *A.*, ii, 561.

PHYSIOLOGICAL CHEMISTRY.

LAST year the death of Wilhelm Pfeffer was recorded; now we regret that of his most prominent pupil, Friedrich Czapek, who had succeeded him as Professor of Botany at Leipzig. Czapek was best known to biochemists through his monumental " Biochemie der Pflanzen," of which the second edition was completed in 1921 by the publication of the third volume. We have further to record the death of Oswald Schmiedeberg, who during the tenure of his chair at Strassburg (1872–1918) trained many of the pharmacologists of to-day. Apart from pharmacology, Schmiedeberg was much interested in physiological chemistry; his most important contribution to this subject was probably his work on chondroitin-sulphuric acid.

It is perhaps no matter for regret that no new journals of biochemical importance have been started during the current year. The outstanding publication, at least as regards size, is the " Handbuch der biologischen Arbeitsmethoden," edited by E. Abderhalden. At the time of writing, more than fifty parts have appeared, on subjects ranging from the preparation of laboratory reagents to the psychology of religion. The work therefore covers a larger field than the " Biochemische Arbeitsmethoden," which it is designed to replace. Whilst parts are excellent, in a compilation by 500 contributors the maintenance of a uniform standard cannot be expected, and biochemists who peruse the work will perhaps not always escape a feeling of disappointment, or possibly of irritation.

Until recently, there were but few original text-books of biochemistry or chemical physiology in English. This year three new ones have appeared, of unequal scope and merit : " Principles of Biochemistry," by Brailsford Robertson, " Biological Chemistry," by H. E. Roaf, and " Biochemistry," by B. Moore. The first-named book deals fully with most aspects of descriptive and dynamic biochemistry, and its value to the advanced student is increased by a select bibliography to each chapter. The second book is of a more elementary character. The third is largely reprinted from original papers by the author; in spite of its title, it only deals with a small portion of the subject. Biochemistry seems as yet too young to have evolved a standard type of text-book. A comparison of English and foreign books on the subject shows a greater disproportion in the treatment of various sub-

divisions than is met with among text-books of organic chemistry, for instance. But possibly this lack of uniformity is inherent in the science, or in its relation to physiology. The increased interest in biochemistry in this country is not only shown by the publication. of new text-books; the subject was much in evidence at the Edinburgh meeting of the British Association.

Of other new books published in 1921, the following may be mentioned : " Applied Colloid Chemistry, General Theory," by W. D. Bancroft; " The Chemistry of Enzyme Action," by K. G. Falk; " Vitamines. Essential Food Factors," by B. Harrow (elementary and semi-popular); " Praktikum der physikalischen Chemie, insbesondere der Kolloidchemie, für Mediziner und Biologen," by L. Michaelis; " Practical Chemical Analysis of Blood," by V. C. Myers (clinical methods); " Organic Medicinal Chemicals," by M. Barrowcliff and F. H. Carr (a practical book concerned with manufacture), and " Organic Compounds of Mercury," by F. C. Whitmore. Nearly all these are American. A second edition of Pfeffer's " Osmotische Untersuchungen " (a reprint) has appeared after a lapse of forty-four years. Attention may be directed to three articles of chemical interest which have appeared in *Physiological Reviews :* " The Carbon Dioxide Carriers of the Blood," by D. D. van Slyke (1921, **1**, 141—176); " The Sugar of the Blood," by J. J. R. Macleod (pp. 208—233); and " Physiological Oxidations," by H. D. Dakin (pp. 394—420). Finally, we may perhaps mention here a new development, which may prove of great convenience to research workers; the firm of Hoffmann-Laroche and Co. has published a catalogue (" Produits biochimiques," Roche) of pure substances of biochemical import- ance, which they are putting on the market; the list comprises amino-acids, proteins, and substances like acetylcholine, colamine, etc., which have not hitherto been obtainable commercially.

Amino-acids and Proteins.

A new general method for synthesising amino-acids, or rather a modification of the well-known Erlenmeyer method, has been described by T. Sasaki,[1] who finds that aldehydes can be con- densed with glycine anhydride (diketopiperazine), which replaces the hippuric acid used by Erlenmeyer. Its condensation product

$$H_2C{\displaystyle \mathop{<}^{CO \cdot NH}_{NH \cdot CO}}CH_2 + 2R \cdot CHO \longrightarrow$$

$$R \cdot CH{:}C{\displaystyle \mathop{<}^{CO \cdot NH}_{NH \cdot CO}}C{:}CHR \xrightarrow[\text{and hydrolysis}]{\text{reduction}} 2R \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$$
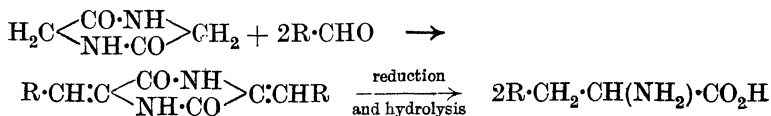
[1] *Ber.,* 1921, **54**, [*B*], 163, 2056; *A.,* i, 196, 808.

with two molecules of aldehyde is readily reduced to the anhydride of a new amino-acid, which is hydrolysed more easily to the amino-acid itself than when hippuric acid is employed. In this way, phenylalanine, tyrosine, dihydroxyphenylalanine, etc., have been prepared, generally in good yield. Mixed anhydrides of glycine and another amino-acid condense with only one aldehyde molecule.[2] Thus dl-leucylglycine anhydride, when heated with benzaldehyde, sodium acetate, and acetic anhydride, yields the substance $C_4H_9 \cdot CH < ^{NAc \cdot CO}_{CO-NH} > C\colon CHPh$, which, by reduction and hydrolysis, should furnish leucylphenylalanine anhydride and a corresponding dipeptide. Unfortunately, extensive racemisation occurs; otherwise this would constitute a valuable method for preparing some of the less accessible dipeptides.

The hydrolysis of gelatin by acids has been studied exhaustively by H. D. Dakin[3] with his new butyl alcohol method;[4] 91·3 per cent. of the protein was isolated as pure amino-acids. It is interesting to compare Dakin's results with those of the first use of the ester method, by Fischer, Levene, and Aders, in 1902. These authors found 16·5 per cent. of glycine, 0·8 per cent. of alanine, 2·1 per cent. of leucine, and 5·2 per cent. of proline; Dakin's figures are respectively 25·5, 8·7, 7·1, and 9·5. Yet Dakin found no new amino-acid in gelatin, indeed one less than Fischer and his co-workers, for valine seems to be absent. A new tricyclic peptide was isolated, γ-*hydroxyprolylproline anhydride*,

$$OH \cdot CH < ^{CH_2 \cdot N - CO \cdot CH \cdot CH_2}_{CH_2 \cdot CH \cdot CO \cdot N - CH_2} > CH_2,$$
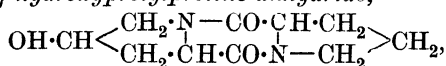
and unidentified sulphur compounds are also present.

A simple new method for the determination of amino-acids has been indicated by R. Willstätter and E. Waldschmidt-Leitz.[5] Their carboxyl groups can be titrated in 97 per cent. alcohol with potassium hydroxide and phenolphthalein as indicator. Similarly, polypeptides can be titrated, even if the alcohol is only 40 per cent.

A curious observation on colostrum has been made by P. E. Howe.[6] The blood of the new-born calf contains neither euglobulin nor pseudo-globulin I, but after it has received colostrum (which is rich in globulin, whereas milk contains scarcely any), the blood contains these two proteins in relatively large amounts. It would appear that the calf receives its first supply of the globulins from the colostrum; if this is withheld, the globulins are only

[2] T. Sasaki and T. Hashimoto, *Ber.*, 1921, **54**, [B], 168; *A.*, i, 197.
[3] *J. Biol. Chem.*, 1920, **44**, 499; *A.*, i, 66.
[4] *Ann. Reports*, 1919, **16**, 153.   [5] *Ber.*, 1921, **54**, [B], 2988.
[6] *J. Biol. Chem.*, 1921, **49**, 115; *A.*, 1922, i, 80.

slowly formed. These observations raise some questions relating to protein assimilation.

J. H. Northrop [7] has compared the hydrolysis of gelatin by pepsin, trypsin, and alkali with a view to determine which linkings are split by each reagent. Those split by the enzymes are also readily split by alkali, but not by acid. Those split by pepsin are also split by trypsin more slowly, but trypsin splits, in addition, other linkings which are not attacked by pepsin. Naturally, the results are somewhat general in character; they are based on the results of formol titration after hydrolysis by one reagent, or by several reagents in succession.

Polysaccharides.

Judging from the numerous publications of last year, the polysaccharides are being more actively investigated than ever before. The interest is shifting from physiological to organic chemistry, and details must be sought in another division of this Report. Here only a few general points can be dealt with. It should be remembered that the first crystalline degradation products of starch, of greater complexity than maltose, were obtained by a biological agent, Schardinger's *Bacillus macerans*.[8]

These crystalline dextrins were investigated by H. Pringsheim,[9] first with A. Langhans and then with F. Eissler; they are di-, tri-, tetra-, and hexa-amyloses, and the molecular weight of their acetyl derivatives in a variety of solvents was found to correspond with the formula $(C_6H_{10}O_5)_n$, where n is respectively 2, 3, 4, or 6. These amyloses give green or reddish-brown, crystalline iodine additive compounds, which dissolve to dark red solutions, and they are not attacked by diastase, saliva, pancreatin, or emulsin, but are hydrolysed by takadiastase and *Penicillium africanum*. It now appears, according to the work of P. Karrer and C. Nägeli,[10] that diamylose is simply an anhydride of maltose, and that methylated starch $\{C_6H_8O_3(OMe)_2\}_x$ has a molecular weight of at most 1200. The aqueous solution of this substance shows the Tyndall effect, but after ultra-filtration with little loss it is optically empty and truly crystalloidal. The conclusion is drawn that the starch molecule contains not more than six dextrose residues united by chemically normal linkings, that is, that it is hexa-amylose polymerised by subsidiary valencies; and that it is related to the amylose as a crystal is to a single molecule. H. Pringsheim

[7] *J. gen. Physiol.*, 1921, **4**, 57; *A.*, i, 823.

[8] *Ann. Reports*, 1912, **9**, 98.

[9] *Ber.*, 1912, **45**, 2533; 1913, **46**, 2959; *A.*, 1912, i, 832; 1913, i, 1156.

[10] *Helv. Chim. Acta*, 1921, **4**, 169, 185, 263; *A.*, i, 310, 311, 313.

and W. Persch [11] conclude (from a study of tetra-amylose) that the methylation of two hydroxyl groups per hexose residue does not cause depolymerisation, which gives additional significance to the molecular weight determinations of the methylation products. Glycogen is also a polymerised amylose, differing from starch in the degree of polymerisation. Karrer and Nägeli believe the molecular weight of starch to be much smaller than it has been supposed to be by various authors, for instance, M. Samec and H. Haerdtl,[12] who have recorded enormous molecular weights for different varieties of starch, up to 260,000.

Inulin is also a relatively simple substance. H. Pringsheim and A. Aronowsky [13] find for the molecular weight of triacetyl-inulin in naphthalene, glacial acetic acid, and phenol a mean value of 2633 corresponding with nine fructose residues, and in agreement with this, P. Karrer and L. Lang [14] deduce from the molecular weight of trimethylinulin that there are eight to ten such residues.

The case of cellulose is complicated by the formation of both cellobiose and dextrose on hydrolysis; one of the questions at issue is the amount of the former sugar present in the molecule. Here, as in the case of other polysaccharides, much may be expected from an application of the methylation methods, which have given Irvine and his pupils such valuable results in the case of the disaccharides.

Nucleic Acids.

A second edition of W. Jones's monograph on this subject has appeared, and H. Morel [15] has also published a useful review dealing with it. Both thymus- and yeast-nucleic acid consist of four nucleotides, each composed of phosphoric acid, sugar, and a base, and the main problem remaining is to determine the way in which these four nucleotides are united by loss of three molecules of water. Until recently, Kossel's suggestion was accepted, that the union is through the phosphoric acid groups. On this view, the nucleic acids would be derivatives of a complex pyrophosphoric acid, that is, acid anhydrides. Levene now considers the union to be between phosphoric acid of one nucleotide and the sugar of another, which would make them esters. Jones, whose views have to some extent been adopted by Thannhauser, imagines

[11] *Ber.*, 1921, **54**, [*B*], 3162.
[12] *Koll. Chem. Beihefte*, 1920, **12**, 281; *A.*, 1921, i, 226.
[13] *Ber.*, 1921, **54**, [*B*], 1281; *A.*, 1921, i, 545.
[14] *Helv. Chim. Acta*, 1921, **4**, 249; *A.*, i, 312.
[15] *Bull. Soc. chim. Biol.*, 1921, **3**, 176.

anhydride formation between the sugar complexes only; hence he regards the nucleic acids as ethers. As there seems to be no way of attacking this problem by synthesis, the experimental work has been mainly concerned with the products obtained by mild hydrolysis, and the rate at which these products are formed. Heating with dilute ammonia is the method most frequently employed, but picric acid,[16] calcium hydrogen sulphite,[17] boiled pancreatic extract,[18] and snake venom [15] have also been used.

In the case of thymus-nucleic acid, the first argument against a linking between the phosphoric acid groups was advanced by P. A. Levene and W. A. Jacobs,[19] who by hydrolysis with 2 per cent. sulphuric acid were able to split off the two purine derivatives, adenine and guanine; the hexose groups to which these bases are attached are also removed, as lævulic acid. The pyrimidine bases are more firmly held and are each obtained attached to one sugar and *two* phosphoric acid groups, as hexocytidine- and hexothymidine-diphosphoric acids, which give barium salts having respectively the formulæ $C_{10}H_{13}O_{12}N_3P_2Ba_2$ and $C_{11}H_{14}O_{13}N_2P_2Ba_2$; these acids have therefore each four acidic hydrogen atoms. Each phosphoric acid grouping must have two free hydroxyl groups and is united to the sugar by its third hydroxyl. If the two phosphoric acid groups were united together, and one were attached to the sugar, three hydroxyl groups would be used up in anhydride formation and only three would be left, so that the diphosphoric acids isolated by Levene and Jacobs would be tribasic instead of tetrabasic. The same acids have been obtained more recently by S. J. Thannhauser and B. Ottenstein,[16] who consider, however, that they are not preformed in thymus-nucleic acid.

Similar arguments have been adduced against the pyrophosphoric acid formula for yeast-nucleic acid. W. Jones [20] has lately attempted to disprove it in another way, by comparing the rates at which phosphoric acid is set free from yeast-nucleic acid and from its four constituent nucleotides. For the entire acid, this rate corresponds with the composite rate calculated for a mixture of the four nucleotides, so that in the formation of these nucleotides by hydrolysis no phosphoric acid group is disturbed. Adenine and guanine are moreover split off from their respective nucleo-

[15] *Bull. Soc. chim. Biol.*, 1921, **3**, 176.

[16] S. J. Thannhauser and B. Ottenstein, *Z. physiol. Chem.*, 1921, **114**, 39; *A.*, i, 521.

[17] H. Steudel and E. Peiser, *ibid.*, 1920, **111**, 297; *A.*, i, 136.

[18] W. Jones, *Amer. J. Physiol.*, 1920, **52**, 203; *A.*, 1920, i, 687.

[19] *J. Biol. Chem.*, 1912, **12**, 411; *A.*, 1912, i, 926.

[20] *Amer. J. Physiol.*, 1920, **52**, 193, 203; *A.*, 1920, i, 687.

tides with equal rapidity, so that the linking cannot be through the purine groups, and by a process of elimination Jones draws the conclusion that the four nucleotides are held together through their sugar complexes. Jones further hydrolysed yeast-nucleic acid with boiled extract of pig's pancreas (which does not contain any active agents other than that hydrolysing yeast-nucleic acid; hence it leaves the thymus acid unaffected). He observed not the slightest increase in acidity, which ought to have occurred if an ester grouping had been broken down, and hence he concludes that the union of the nucleotides is between two sugar groups, that is, yeast-nucleic acid is an ether.

Levene, on the other hand, adheres to the ester linking between the phosphoric acid of one nucleotide and the sugar grouping of another. He [21] considers this to be supported by Jones's experiments on the rate of hydrolysis, which, in his opinion, merely indicate that the union of the four nucleotides is more labile than that between the phosphoric acid and (its own) sugar. The increase in acidity due to the breakdown of the ester grouping does not show itself owing to buffer effect. He formulates thymus-nucleic acid as follows :

$$
\begin{array}{l}
\qquad\qquad\qquad\text{H}\\
\text{HO·CH}_2\text{·CH·CH·[CH·OH]}_2\text{·C·C}_5\text{H}_4\text{N}_5\\
\qquad\quad |\quad\ |\ \text{-----O-----}\ |\quad\text{adenine group}\\
\qquad\quad \text{O}\\
\quad\ \ \text{O}\!\!>\!\!\text{P·O·CH}_2\text{·CH·CH·[CH·OH]}_2\text{·C·C}_5\text{H}_5\text{O}_2\text{N}_2\\
\text{HO}\quad\ \ |\quad |\text{------O------}|\quad\text{thymine group}\\
\qquad\qquad\text{O}\qquad\qquad\qquad\qquad\text{H}\\
\qquad\ \ \text{O}\!\!>\!\!\text{P·O·CH}_2\text{·CH·CH·[CH·OH]}_2\text{·C·C}_5\text{H}_4\text{ON}_5\\
\quad\ \ \text{HO}\quad |\quad\ |\text{------O-----}|\ \text{guanine group}\\
\qquad\qquad\quad\text{O}\qquad\qquad\qquad\quad\text{H}\\
\qquad\qquad\ \ \text{O}\!\!>\!\!\text{P·O·CH}_2\text{·CH·CH·[CH·OH]}_2\text{·C·C}_4\text{H}_4\text{ON}_3\\
\qquad\quad\ \text{HO}\quad |\quad\ |\text{----O-----}|\ \text{cytosine group}\\
\qquad\qquad\qquad\quad\text{O}\\
\qquad\qquad\qquad\ \ \text{O}\!\!>\!\!\text{P·OH}\\
\qquad\qquad\qquad\text{HO}
\end{array}
$$
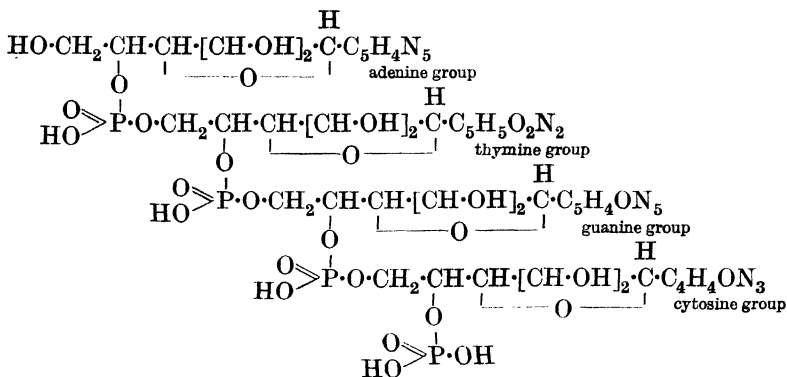
The arrangement of the basic groups is, of course, to some extent arbitrary, but as thymine and cytosine can be obtained with one sugar and two phosphoric acid groups attached (see above), they cannot both be in the same half of the molecule. Levene has given a similar formula for yeast-nucleic acid.[22] By way of comparison Jones's formula [23] for this acid may be given.

[21] J. Biol. Chem., 1921, **48**, 119; A., i, 821.

[22] Ibid., 1919, **40**, 415; A., 1920, i, 193.

[23] Amer. J. Physiol., 1920, **52**, 203; A., 1920, i, 687.

$$O{:}P(OH)_2{\cdot}O{\cdot}C_5H_7O_2{\cdot}C_4H_3O_2N_2$$

$$\underset{O}{|} \quad \text{uracil group}$$

$$O{:}P(OH)_2{\cdot}O{\cdot}C_5H_6O{\cdot}C_5H_4N_5$$

$$\underset{O}{|} \quad \text{adenine group}$$

$$O{:}P(OH)_2{\cdot}O{\cdot}C_5H_6O{\cdot}C_4H_4ON_3$$

$$\underset{O}{|} \quad \text{cytosine group}$$

$$O{:}P(OH)_2{\cdot}O{\cdot}C_5H_7O_2{\cdot}C_5H_4ON_5$$

$$\text{guanine group}$$
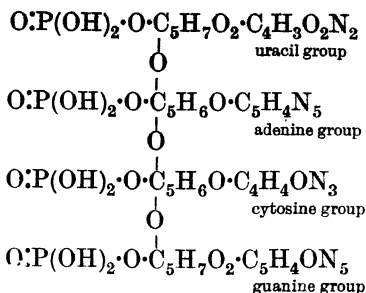
Finally, we may indicate the present position of the chemical technique of this subject. All the four nucleotides constituting yeast-nucleic acid have been crystallised in the free state; [24] their salts are more readily obtained crystalline. In the case of thymus-nucleic acid, the labile attachment of the purine groups and the instability of their hexose residues have prevented the same result from being obtained. Here the furthest advance is marked by the barium salt of hexothymidine-diphosphoric acid, the most complex degradation product of nucleic acid which has so far been crystallised. Alleged di- and tri-nucleotides [25] have on further investigation proved to be mixtures of mono-nucleotides.[26]

Ferments and Fermentation.

Various investigators have at different times suggested that ferment action is preceded by the formation of a complex with the substrate, which formation may require the presence of electrolytes. That this is so in the case of amylase has recently been shown by L. Ambard [27] in a paper of considerable interest. Powdered starch removes amylase from solution and keeps it fixed, in spite of repeated washing in the centrifuge. On the other hand, it gives up the ferment promptly to filtered starch and to glycogen solutions containing neutral salt; the latter process the author terms " défixation." It furnishes a convenient method for estimating amylase (in saliva, blood, urine, etc.); 96—100 per cent. of the ferment in a solution may be removed by starch

[24] P. A. Levene, *J. Biol. Chem.*, 1920, **41**, 483; *A.*, 1920, i, 452.

[25] P. A. Levène and W. A. Jacobs, *ibid.*, 1912, **12**, 411; *A.*, 1912, i, 926. W. Jones and H. C. Germann, *ibid.*, 1916, **25**, 93; *A.*, 1916, i, 515. S. J. Thannhauser and G. Dorfmüller, *Z. physiol. Chem.*, 1917, **100**, 121; *A.*, 1918, i, 47.

[26] Compare, respectively, P. A. Levene, *J. Biol. Chem.*, 1921, **48**, 119; *A.*, i, 821. W. Jones and A. F. Abt, *Amer. J. Physiol.*, 1920, **50**, 574; *A.*, 1920, i, 687. P. A. Levene, *J. Biol. Chem.*, 1920, **43**, 379; *A.*, 1920, i, 774.

[27] *Bull. Soc. chim. Biol.*, 1921, **3**, 51; *A.*, i, 368.

powder, which is then mixed with filtered starch solution containing sodium chloride and a phosphate mixture (to maintain the optimal P_H 6·6). After keeping at 35° for a time, during which at most one-tenth of the starch is hydrolysed (and the rate is still constant), the action is stopped by alkali, and the maltose is estimated by Bertrand's process. Whether solid starch requires salt for the fixation of amylase could not be established, for the solid starch cannot be washed free from salt. Salt-free glycogen " defixes " only 4 per cent., but on addition of salt, 98 per cent. The change of P_H to 5·0 or to 8·0 had no effect on defixation, but caused in either case a fall of 40 per cent. in the rate of hydrolysis, which is due only to a very slight extent to destruction of the ferment.

The effect of various salts on diastase action has been often investigated, recently again by W. Biedermann,[28] who calls the salt a co-ferment and finds that the effect of the anion predominates; sodium chloride is the most active, followed closely by potassium thiocyanate. Nitrates, iodides, and sulphates are much less active; evidently the effect is a lyotropic one. A. Hahn and R. Michalik [29] consider, in the case of pancreatic diastase, that the activation by salts is a diminution in the size of the colloidal enzyme particles.

Something similar to Ambard's " défixation " had been observed before in the case of invertase adsorbed on ferric hydroxide, which O. Meyerhof [30] found to be as active in a sucrose solution as the same amount of unadsorbed ferment. E. G. Griffin and J. M. Nelson [31] showed the same to be true when charcoal is the adsorbent; it is only necessary to maintain the proper hydrogen-ion concentration, which is upset by charcoal (this point had been neglected in earlier experiments, by Eriksson on invertase, and by Hedin on rennet). Lately, L. Michaelis [32] has described a quantitative confirmation of Meyerhof's experiments, in an interesting paper dealing with the theory of invertase action. Invertase adsorbed on ferric hydroxide cannot be removed by washing with water; it is slowly removed by sucrose, maltose, and raffinose solutions, but not by lactose, dextrose, fructose, mannose, or α- or β-methylglucoside. Although invertase adsorbed on ferric hydroxide is evidently colloidal, Michaelis concludes that the kinetics of a homogeneous system still hold good. The adsorbed invertase

[28] *Fermentforsch.*, 1920—1921, **4**, 258; *A.*, i, 468.

[29] *Z. Biol.*, 1921, **73**, 10; *A.*, i, 282.

[30] *Pflüger's Archiv*, 1914, **157**, 251; *A.*, 1914, ii, 450.

[31] *J. Amer. Chem. Soc.*, 1916, **38**, 722, 1109; *A.*, 1916, i, 439, 516.

[32] *Biochem. Z.*, 1921, **115**, 269; *A.*, i, 468.

molecules must all be on the surface of the ferric hydroxide, and are equally active.

The adsorption of invertase by various reagents has recently been utilised by R. Willstätter and F. Racke [33] for the purification of the enzyme. This work is part of an important investigation of enzymes, begun by Willstätter with a view to their preparation in as pure a state as possible.

The extraction of invertase from yeast by digestion with water is by no means a purely physical process; preliminary autolysis is apparently necessary. The manner in which the yeast has been dried and the addition of antiseptics both affect the process. The crude extract is purified by adding a limited amount of kaolin, which principally adsorbs impurities. The invertase is then adsorbed on aluminium hydroxide, from which it cannot be removed by water, but almost quantitatively by 1 per cent. aqueous disodium hydrogen phosphate, 0·04 per cent. aqueous ammonia, very dilute sodium carbonate, or aqueous pyridine. Invertase decomposes spontaneously in aqueous solution and becomes quite inactive in a year and a half. Previously Willstätter [34] had investigated peroxydases. A feature of the extraction of the latter from horse-radish is the prolonged intensive dialysis of thin slices of the root, which is subsequently killed by dilute oxalic acid, and thus the enzyme is set free from the cells. After concentration of the extract, the peroxydase is precipitated by alcohol. In order to control the various operations, a method of estimation has been worked out, depending on the amount of purpurogallin formed (ascertained colorimetrically). After precipitation by alcohol and purification by mercuric chloride, the best specimens were about 2500 times as active as powdered horse-radish. Later, by adsorption on aluminium hydroxide from 50 per cent. alcohol, and recovery by extraction with water containing carbonic acid, the activity of the preparation was nearly doubled. The purest specimens seem to consist chiefly of a nitrogenous glucoside containing more than 30 per cent. of a pentose and an equimolecular proportion of a hexose, with three atomic proportions of nitrogen.

L. Michaelis and M. Rothstein [35] have investigated the rate of destruction of rennet and pepsin at various temperatures by different hydroxyl-ion concentrations. Under all conditions, the rate for the two enzymes is in constant proportion. The rate of

[33] *Annalen*, 1921, **425**, 1; *A.*, i, 823.

[34] R. Willstätter and A. Stoll, *ibid.*, 1918, **416**, 21; *A.*, 1918, i, 555. R. Willstätter, *ibid.*, 1921, **422**, 47; *A.*, i, 138.

[35] *Biochem. Z.*, 1920, **105**, 60; *A.*, 1920, i, 775.

destruction is proportional to the 1·5th power of the amount of enzyme present and to the fourth power of the hydroxyl-ion concentration. The destruction begins when P_H exceeds 6.

Alcoholic fermentation was last fully dealt with in these Reports two years ago, particularly in regard to the second form of fermentation which produces glycerol according to the equation :

$$C_6H_{12}O_6 = CH_3 \cdot CHO + CO_2 + C_3H_8O_3.$$

Later, C. Neuberg and J. Hirsch [36] distinguished a third form, in which the acetaldehyde is " dismuted " into alcohol and acetic acid, as follows :

$$2C_6H_{12}O_6 + H_2O = CH_3 \cdot CO_2H + C_2H_5 \cdot OH + 2C_3H_8O_3 + 2CO_2.$$
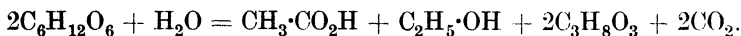
The proportions of the products demanded by the above equation have been verified experimentally. In the second form, the acetaldehyde is " trapped " by an alkaline sulphite; the third form occurs in the absence of sulphite, when a feebly alkaline reaction is maintained by potassium carbonate, magnesium oxide, or an alkaline phosphate. Neuberg considers that in all varieties of fermentation pyruvic acid is first formed and is then decarboxylated to acetaldehyde; these two substances occupy a central position in the various schemes. The aldehyde may be trapped by other means than alkaline sulphites. The same object may be attained by dimethyl*cyclo*hexanedione [37] (dimethyldihydroresorcinol), two molecules of which condense with one of acetaldehyde to form the substance

$$
\begin{array}{ccc}
 & \underset{|}{CH_3} & \\
CO & CH & CO \\
\diagup\;\diagup & & \diagdown\;\diagdown \\
H_2C\quad CH & HC & CH_2 \\
Me_2C\quad CO & OC & CMe_2 \\
\diagdown\;\diagdown & & \diagup\;\diagup \\
CH_2 & & CH_2
\end{array}
$$
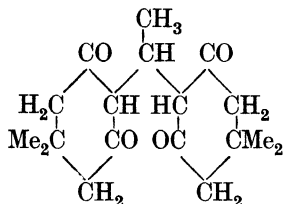
Lately, M. von Grab [38] has been able to fix pyruvic acid itself by means of a biochemical Döbner synthesis of α-methyl-β-naphthacinchonic acid.

$$
\begin{array}{cccc}
CH_3 \cdot CO \cdot CO_2H & & CH_3 \cdot C{:}N & + 2H_2O \\
 & + \underset{C_{10}H_7}{H_2N\diagdown} = & \underset{HC{:}C \cdot CO_2H}{\overset{|}{\quad}{>}C_{10}H_6} & + CO_2 + H_2 \\
CH_2{:}C(OH) \cdot CO_2H & & &
\end{array}
$$
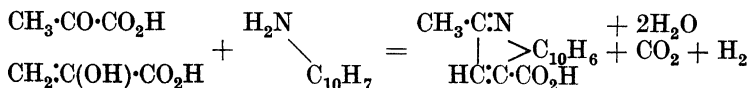
[36] *Biochem. Z.*, 1919, **100**, 304; *A.*, 1920, i, 798.

[37] C. Neuberg and E. Reinfurth, *ibid.*, 1920, **106**, 281; *A.*, i, 914.

[38] Quoted by Neuberg in a useful résumé in *Festschr. d. Kaiser Wilhelm Gesellsch. z. Förderung d. Wissensch. zu ihrem 10-jährigen Jubiläum*, Berlin, 1921, 169.

The central position of acetaldehyde is further revealed by " trapping " it in other fermentations, due to bacteria and moulds. Thus acetaldehyde is an intermediate product in the fermentation of sugar by *B. lactis aerogenes*[39] and by *Aspergillus, Mucor, Monilia,* and *Oidium.*[40] Moulds decompose pyruvic acid with the formation of acetaldehyde.[41]

W. H. Peterson and E. B. Fred[42] have applied the sulphite fixation method to pentose-fermenting organisms (*B. acetoethylicus* and *Lactobacillus pentoaceticus*). The largest yield was from xylose. The first-named organism also produces acetone, which is perhaps formed from the acetaldehyde by successive condensation, oxidation, and decarboxylation.

Normally, in bacterial fermentations the acetaldehyde is dismuted into alcohol and acetic acid, and the hydrogen, not finding an acceptor, escapes as such; that is, no glycerol is formed. This happens, for instance, in butyric acid fermentation, and Neuberg and Arinstein[43] have shown recently that pyruvic acid and acetaldehyde are here also intermediate products. An aldol-condensation product of the former substance is considered to undergo decarboxylation and rearrangement to butyric acid, the nett result being

$$C_6H_{12}O_6 = 2CO_2 + 2H_2 + C_4H_8O_2.$$
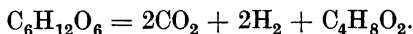
This Neuberg calls a fourth variety of fermentation.

The number of enzymes known to occur in yeast is considerable. Yet an enzyme of a novel type has been discovered in *carboligase*,[44] present in maceration juice and so called because it links carbon atoms. The phytochemical reduction of benzaldehyde by yeast results in the formation of benzyl alcohol and, in addition, a hydroxy-ketone of the constitution $CH_3 \cdot CH(OH) \cdot CO \cdot C_6H_5$ (or possibly $CH_3 \cdot CO \cdot CH(OH) \cdot C_6H_5$), which is considered to be formed from benzaldehyde and acetaldehyde by a benzoin condensation. Apart from its numerous enzymes, yeast is very complex in the manner in which fermentation is accelerated or inhibited by various conditions. O. Meyerhof[45] observed that when sugar is added to maceration extract there is an induction period, during which no sign of fermentation is observable, but the induction period

[39] C. Neuberg, F. F. Nord, and E. Wolff, *Biochem. Z.*, 1920, **112**, 144; *A.*, i, 148.

[40] C. Cohen, *ibid.*, 139; *A.*, i, 150.

[41] T. Nagayama, *ibid.*, 1921, **116**, 303; *A.*, i, 836.

[42] *J. Biol. Chem.*, 1920, **44**, 29; *A.*, 1920, i, 911.

[43] Quoted from Neuberg's résumé, *loc. cit.* (reference [38]).

[44] C. Neuberg and J. Hirsch, *Biochem. Z.*, 1921, **115**, 282; *A.*, i, 480.

[45] *Z. Physiol, Chem.*, 1918, **102**, 185; *A.*, 1919, i, 57.

is abolished by a trace of hexose phosphate. Disodium hydrogen phosphate affects the interval which elapses before maximal fermentation is attained, and other salts, such as sodium chloride, do the same. The induction period is shortened by the addition of aldehydes and of pyruvic acid (Oppenheimer, Neuberg), which function as hydrogen acceptors. The formation of pyruvic acid from dextrose apparently requires the presence of a hydrogen acceptor, which is normally acetaldehyde, derived from the earlier stage of the reaction. The fermentation is therefore autocatalytic. That a hydrogen acceptor is wanting in the induction period was shown by A. Harden and F. R. Henley,[46] who could shorten the induction period by adding methylene-blue. Lævulose can somewhat hasten the fermentation of dextrose, but acetaldehyde is fifty times as effective. Harden and Henley have also confirmed the salt effect observed by Meyerhof.

As is well known, hexose phosphate has an enormous effect on the course of fermentation. A purely chemical effect which is probably analogous, has been discovered by E. J. Witzemann,[47] who finds that the oxidation of dextrose to carbon dioxide by hydrogen peroxide is catalysed by disodium hydrogen phosphate; the intermediate formation of a hexose phosphate could not, however, be demonstrated in these experiments. A further purely chemical analogy of another phase of alcoholic fermentation is described by E. Müller;[48] finely divided osmium decomposes neutral formaldehyde solution according to the equation :

$$3H_2CO + H_2O = CO_2 + 2CH_3 \cdot OH.$$
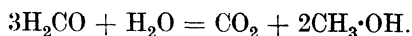
Tissue Oxidation.

The reduction of organic substances by nickel at a high temperature, according to Sabatier and Senderens, is a reversible process, and this induced H. Wieland[49] to postulate the same reversibility for Paal's process of reduction at the ordinary temperature by palladium. He was able to show that in the complete absence of oxygen, quinol is partly dehydrogenated by palladium black to p-benzoquinone; dihydronaphthalene is partly oxidised, partly reduced, to a mixture of naphthalene and tetrahydronaphthalene, after the manner of the Cannizzaro (mutase) reaction. The

[46] Biochem. J., 1920, 14, 642; A., 1920, i, 914; ibid., 1921, 15, 175, 312; A., i, 480, 642.
[47] J. Biol. Chem., 1920, 45, 1; A., i, 160.
[48] Ber., 1921, 54, [B], 3214.
[49] Ibid., 1912, 45, 484; 1913, 46, 3327; 1914, 47, 2085. Compare also H. G. Denham, Z. physikal. Chem., 1910, 72, 641; A., 1910, ii, 598.

palladium finally contains hydrogen and soon becomes inactive, unless the hydrogen be removed by an "acceptor," which may be methylene-blue, *p*-benzoquinone, or simply oxygen. Later, Wieland interpreted as dehydrogenation also reactions, which are apparently true oxidation (addition of oxygen). He considers the conversion of an aldehyde to an acid as the removal of two hydrogen atoms from the hydrated form of the aldehyde :

$$\text{R·C} {\overset{\displaystyle /\text{OH}}{\underset{\displaystyle \backslash\text{H}}{\text{—OH}}}} \longrightarrow \text{R·C:O} {\overset{\displaystyle /\text{OH}}{}} + \text{H}_2$$
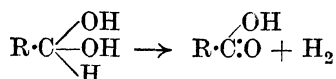
Thus formic acid was shown to be an intermediate stage in the oxidation of carbon monoxide to the dioxide.

Starting from this basis, Wieland attempted to explain biological oxidations in the same way. Glucose is partly oxidised by palladium black at the ordinary temperature to carbon dioxide, and the palladium is found to be charged with hydrogen. If *p*-benzoquinone or methylene-blue be added as hydrogen "acceptor," the oxidation proceeds further; 14 per cent. of the glucose was completely burnt to carbon dioxide in one experiment, and with oxygen at 40°, 20 per cent. was completely oxidised. Phenols and other substances which are generally regarded as substrates for an oxydase or peroxydase are likewise oxidised by palladium, which is thereby charged with hydrogen, but tyrosine and uric acid are not affected, so that palladium does not imitate the action of tyrosinase or uricase, which probably are associated with a hydrolytic ferment, absent in the palladium. Ethyl alcohol may be oxidised to acetic acid by means of palladium and *p*-benzoquinone, in the complete absence of free oxygen :

$$\text{CH}_3\text{·CH}_2\text{·OH} + \text{H}_2\text{O} + 2\text{C}_6\text{H}_4\text{O}_2 = \text{CH}_3\text{·CO}_2\text{H} + 2\text{C}_6\text{H}_4(\text{OH})_2.$$
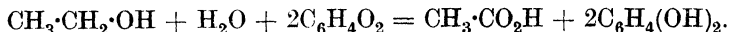
The palladium may be replaced by *Bacterium aceti*, the quinone by methylene-blue, and still oxidation takes place without elementary oxygen intervening. The action of the Schardinger ferment, which reduces methylene-blue in the presence of aldehydes, and the aldehyde mutase of Parnas, which makes aldehydes undergo the Cannizzaro reaction, can all be regarded from the same point of view. The same ferment (dehydrase) in milk can (1) oxidise salicylaldehyde to the acid in the presence of free oxygen, which is then the hydrogen acceptor; (2) in the absence of oxygen act as mutase; half the aldehyde is oxidised, and the other half, acting as acceptor, is reduced to saligenin; (3) in the presence of methylene-blue as acceptor, the aldehyde is only reduced.

Wieland has since apparently abandoned the above line of research, which is now attracting the attention of physiologists,

rather than of organic chemists. In particular, his ideas have been adopted by T. Thunberg in a remarkable paper [50] on intermediate metabolism. Thunberg has studied the effect of a large number of organic substances on the decoloration of methylene-blue by muscle.

Fresh frog's muscle is cut up very fine and extracted several times with distilled water, in order to remove a substance which by itself reduces methylene-blue. When the muscle has thus been completely inactivated, as little as 0·2 gram is introduced into a " vacuum tube " with 0·02 mg. (about 0·05 millimole) of methylene-blue and a considerable excess (400—800 equivalents) of the substance under investigation. After making the mixture up to 1 c.c., the tube is completely evacuated, filled with water, placed in a thermostat, and inspected at intervals for decoloration. If the substance is a " donator " of hydrogen, the latter is transferred by an enzyme of the muscle (" hydrogen transportase ") to the methylene-blue. According to the author, all nutrient material must be able to yield up hydrogen, which is the universal primary fuel of the cell. A substance which does not give up hydrogen cannot be an intermediate metabolite. Hence methylene-blue can be used in order to test substances for their possible significance in intermediate metabolism. There are pronounced differences, even between the members of a homologous series; formic, acetic, butyric, and hexoic acids will give up hydrogen; propionic, isobutyric, and isovaleric acids will not.

Succinic acid is most active and by means of methylene-blue as little as 0·02 mg. of the acid may be detected and estimated.[51] Fumaric acid also gives up hydrogen, but much less readily; the latter reaction is reversible; some methylene-blue remains unreduced, however little be taken, for the acetylenedicarboxylic acid formed enters into competition with the methylene-blue for the hydrogen :

fumaric acid + methylene-blue $\xrightarrow{\longleftarrow}$ acetylenedicarboxylic acid
+ leucobase.
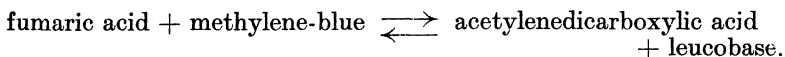
Among hydroxy-acids, glycollic and α-hydroxyisobutyric acids are inactive, but lactic and α- and β-hydroxybutyric acids are oxidised. Their dehydrogenation doubtless results in the formation of an unsaturated hydroxy-acid tautomeric with the keto-acid. As an illustration of the application of the method to metabolic problems, Thunberg suggests that as α- and 'β-hydroxybutyric acids are about equally ready hydrogen donators, the former acid may also be a product of intermediate metabolism.

[50] Skand. Arch. Physiol., 1920, 40, 1; A., 1920, i, 784.
[51] Svenska Läkareförenigenshandlingar, 1917, 43, 996; A., 1918, ii, 87,

Among the amino-acids examined, glutamic is the most active, alanine has some effect, but various others are inactive. The removal of hydrogen is considered to lead to an imino-acid, which in turn forms the keto-acid, now fully recognised as the first non-nitrogenous degradation product of amino-acids.

The question naturally arises whether the dehydrogenation of so many diverse substances is effected by one and the same enzyme, or by different ones. Experiments on the destruction by cold, and by heat, led Thunberg to the suggestion that the enzymes are different, the one acting on succinic acid being the most stable. Yet the possibility does not seem excluded, that in Thunberg's destruction experiments only enough of a single enzyme survived to dehydrogenate the most sensitive succinic acid, but not to attack other substances, from which hydrogen is removed less readily.

A most important advance in the investigation of tissue oxidation has been made by F. G. Hopkins,[52] who has isolated an autoxidisable cell constituent, which has the catalytic properties of a co-enzyme. It is interesting to observe how scientific investigations, at first widely apart, may ultimately converge on the same problem. De Rey-Pailhade [53] first showed that extracts of yeast and of many animal tissues reduce sulphur to hydrogen sulphide. They contain therefore, in Thunberg's parlance, a hydrogen donator, which De Rey-Pailhade regarded as a " hydride of protein " and named *philothion*. Hopkins has now shown this substance to be a dipeptide of cysteine and glutamic acid, and calls it *glutathione*. Its isolation was rendered possible by Mörner's delicate nitroprusside reaction for cysteine, which reaction Heffter, and afterwards V. Arnold,[54] showed to be given by many tissue extracts. Using this reaction as a guide, Hopkins, by a very complicated process, obtained glutathione, in a yield of 0·01—0·02 per cent. of the fresh tissue employed, from yeast, from muscle, and from mammalian liver. The nitroprusside reaction is also given by proliferating plant tissues, bacteria, and nearly all animal tissues, but not by connective-tissue, nor by blood plasma. The reaction is not given by the fowl's egg, but is given by a thirty-hours' embryo. Glutathione was mostly analysed in the oxidised (disulphide or cystine) form, $C_{16}H_{26}O_{10}N_4S_2$; the thiol form, $C_8H_{14}O_5N_2S$, was obtained crystalline. This dipeptide is quite resistant to proteolytic enzymes, but is hydrolysed by boiling acids to equimolecular proportions of cystine and glutamic acid. The

[52] *Biochem. J.*, 1921, **15**, 286; *A.*, i, 635.
[53] *Compt. rend.*, 1888, **106**, 1683; **107**, 43; *A.*, 1888, 1101.
[54] *Z. physiol. Chem.*, 1911, **70**, 300; *A.*, 1911, i, 306.

outstanding position of the latter among amino-acids in Thunberg's experiments has already been referred to above.

Hopkins is especially concerned with showing that glutathione exercises real functions in the chemical dynamics of the cell. As in the case of other thiol compounds, the oxidation to the disulphide form depends greatly on the hydrogen-ion concentration. In neutral or slightly alkaline solution, it is oxidised spontaneously by air, but in acid solution it is a less ready donator of hydrogen and is more stable. The oxidised form, on the other hand, is a hydrogen acceptor; fresh tissues placed in a solution of the oxidised form reduce it, as shown by the development of the nitroprusside reaction. Fresh tissues also reduce methylene-blue (as was pointed out above in discussing Thunberg's work), but when they have been kept sufficiently long for their reduction potential to have fallen, so that methylene-blue is no longer reduced, they now oxidise the reduced dipeptide under anaerobic conditions, so that some other substance must act as hydrogen acceptor. The converse reaction, reduction of the disulphide form, depends greatly on the hydrogen-ion concentration. In slightly acid solutions ($P_H <$ or $= 6·8$), the disulphide form simply competes with methylene-blue for the reducing action of fresh tissues, and as a result, the normal rate of decoloration of the methylene-blue is slowed. In slightly alkaline solution ($P_H >$ or $= 7·4$), the rate of decoloration is greatly accelerated by the addition of oxidised peptide, which now functions catalytically like a co-enzyme. Herein it differs from succinic acid and the other substances investigated by Thunberg, which are dehydrogenated irreversibly. The reversibility of the action of glutathione is closely connected with its thiol grouping. The autoxidation of this group in cysteine and other compounds has been studied by A. P. Mathews and S. Walker [55] and by T. Thunberg; [56] it is much influenced by catalysts.

During the year two reviews on physiological oxidation have appeared; the one, by Dakin, is referred to in the introduction; the other is by P. Woringer and occupies the September number of the *Bulletin de la Société de chimie biologique* (1921, **3**, 311—450).

The Chemistry of Muscular Contraction.

We are still very ignorant of the way in which the muscle transforms chemical into mechanical energy. The source of the former is some carbohydrate, glycogen, or its fission product

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[55] *J. Biol. Chem.*, 1909, **6**, 289; *A.*, 1909, i, 698.
[56] *Skand. Arch. Physiol.*, 1913, **30**, 285; *A.*, 1914, i, 386.

dextrose, and the presence in muscle of lactic acid (isomeric with a triose) suggested that it had something to do with the energy transformation. Nevertheless, lactic acid accumulates in the living muscle only after violent exertion, and then only to a slight extent, so that there must be a mechanism for its rapid removal. Some interesting light on the origin of lactic acid from carbohydrates has been obtained by G. Embden and his pupils, who found [57] that muscle press juice contains a substance capable of generating lactic acid, which they called *lactacidogen*. Later,[58] they described the preparation, in a yield of 0·05 per cent. of the muscle employed, of an osazone identical with that previously obtained by A. von Lebedeff [59] and W. J. Young [60] from yeast and recognised as derived from hexose phosphoric acid.

Whether lactacidogen itself is quite identical with the co-enzyme of alcoholic fermentation is not decided, but at any rate the two substances are closely related, and there are some points of similarity between the methods of degradation of the glucose molecule in muscle and in yeast. This similarity has also been insisted on by O. Meyerhof,[61] who found that extracts of muscle contain the co-enzyme of alcoholic fermentation and that this substance plays a part in the respiration and energy transformation in the muscle. Embden and his co-workers have more recently examined the effect of a large number of physiological factors on the lactacidogen content of muscle; a whole number of the *Zeitschrift für physiologische Chemie* [62] was exclusively devoted to these researches. Some of the main conclusions are as follows. Where muscular activity is greatest, there is most lactacidogen. Frogs contain more at 30° than at 0°, and the increase in lactacidogen is accompanied by a decrease of residual phosphorus. The synthesis of lactacidogen is not under nervous control. The white muscles of rabbits contain about twice as much as the more sluggish red ones, which latter, on the other hand, are richer in non-lactacidogen phosphorus, which is regarded as in reserve. Muscular work and strychnine convulsions decrease the lactacidogen in the white muscles of the rabbit, but not in the red, where, owing to slower action, time is given for its re-synthesis. Since both carbohydrate and phosphoric acid are necessary for the production of lactacidogen, the idea suggested itself of adminis-

[57] *Biochem. Z.*, 1912, **45**, 45, 63; *A.*, 1912, ii, 1071, 1072.
[58] *Z. physiol. Chem.*, 1914, **93**, 1; 1917, **100**, 181; 1921, **113**, 1; *A.*, 1915, i, 344; 1917, i, 674; 1921, i, 528.
[59] *Biochem. Z.*, 1909, **20**, 114; *A.*, 1909, i, 863. .
[60] *Ibid.*, 1911, **32**, 177; *A.*, 1911, i, 422.
[61] *Z. physiol. Chem.*, 1918, **101**, 165; **102**, 1; *A.*, 1918, i, 242, 464.
[62] 1921, **113**, 1—312; *A.*, i, 528—530.

tering phosphate in order to increase the capacity for work. Numerous experiments on soldiers (with an ergostat and by marching) and on miners are recorded [63] in which 7·5 grams of sodium dihydrogen phosphate per day by the mouth is said to have increased the capacity for muscular work.

O. Meyerhof [64] has stated the view that the transformation of hexose to lactic acid is reversible, according to the following scheme :

hexosediphosphoric acid $+ 2H_2O = 2$ lactic acid $+ 2$ phosphoric acid

3 lactic acid $+ 2$ phosphoric acid $+ 3O_2 = 3CO_2 + 5H_2O +$
$$1 \text{ hexosediphosphoric acid.}$$
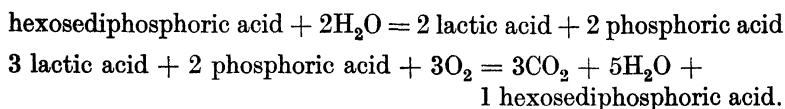
W. Hartree and A. V. Hill [65] have studied the same problem by a purely physical method, measurement of the rate of heat production in a stimulated frog's muscle at different temperatures. The temperature coefficient is 2·8 for 10° and previously the rate of relaxation was shown to have a coefficient of 2·2, so that both processes are purely chemical (the energy liberated by the change from dextrose to lactic acid is only about 16 per cent. of the heat given out, but the 84 per cent. is derived from potential energy due to the effect of lactic acid on some " active " structure or surface). The observations suggest to the authors the mechanical analogy of a large reservoir of compressed air, connected by a narrow tube with an elastic bag with a release valve. When the valve is opened, the air rushes out, at first rapidly and then more slowly until the rate of outflow reaches a value determined by the bore of the connecting tube. Chemically, the large reservoir of energy is the store of glycogen in the muscle, the narrow tube is a catalyst, transforming the glycogen into lactic acid. (The administration of phosphate in Embden's experiments, described above, would be an attempt to widen the tube.) The elastic bag is represented by the balanced action, carbohydrate $\rightleftharpoons$ lactic acid. The opening of the bag is represented by a temporary permeability to lactic acid, produced by the stimulus in some membrane. The lactic acid escapes and causes a change in colloidal properties, resulting in contraction of the muscle-fibres. In the later stages of prolonged stimulation the lactic acid is removed at the same rate at which it is supplied, and a dynamic equilibrium is established, corresponding with the steady production of heat (which has the temperature coefficient of 2·8 per 10°).

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[63] G. Embden, E. Grafe, and E. Schmitz, Z. physiol. Chem., 1921, 113, 67; A., i, 529.

[64] Pflüger's Archiv, 1920, 182, 232, 284; A., i, 76.

[65] J. Physiol., 1921, 55, 133; A., i, 527.

Accessory Food Substances and Calcium Metabolism.

A method of estimating the vitamin-*B* content of a solution by its effect on the growth of yeast, as suggested by Williams and others,[66] has been further criticised by various authors, who find that yeast can synthesise this vitamin. V. E. Nelson, E. I. Fulmer, and R. Cessna [67] subcultured a yeast on alternate days throughout a year by adding 1 c.c. of the culture to 50 c.c. of a solution containing only salts and sucrose. The maximum concentration of the original constituents was thus 1×50^{-180}. Yet at the end of the year the yeast contained enough vitamin-*B* for the normal growth of rats. Similar conclusions were drawn by M. R Mac-Donald and E. V. McCollum [68] and by A. Harden and S. S. Zilva; [69] the latter authors showed the presence of vitamin-*B* by its curative effect on polyneuritis in pigeons.

Since we are as yet completely ignorant of the chemical nature of vitamins, the observation by S. S. Zilva and M. Miura [70] is of some interest, that both the antineuritic and the antiscorbutic vitamins diffuse through a collodion membrane of such permeability as permits the passage of methylene-blue, neutral-red, safranine, and other semi-colloids. The fact that vitamin-*A* is destroyed by atmospheric oxygen,[71] particularly at high temperatures, has been further confirmed,[72] and exposure to ozone has been found to have the same effect.[73]

During the year the main interest in vitamins has, however, shifted to the anti-rachitic substance and its connexion with calcium metabolism, which is leading to some new points of view. E. Mellanby [74] has published in detail his extensive researches on the production of experimental rickets in dogs. He has dieted nearly four hundred puppies and draws the conclusion that among the conditions which induce rickets the most important are a deficiency, in the diet, of calcium and phosphorus and of fat containing the anti-rachitic vitamin. Since the effect of fats in promoting growth runs parallel to their effect in preventing rickets, it is highly probable that the anti-rachitic vitamin is identical with vitamin-*A*. Thus butter fat, through which oxygen is bubbled

[66] *Ann. Reports*, 1920, **17**, 167.

[67] *J. Biol. Chem.*, 1921, **46**, 77; *A.*, i, 386.

[68] *Ibid.*, 1920, **45**, 307; A., i, 480.   [69] *Biochem. J.*, 1921, **15**, 438; *A.*, i, 702.

[70] *Ibid.*, 422; *A.*, i, 702.   [71] *Ann. Reports*, 1920, **17**, 165.

[72] F. G. Hopkins, *Biochem. J.*, 1920, **14**, 725. J. C. Drummond and K. H. Coward, *ibid.*, 734; *A.*, i, 475.

[73] S. S. Zilva, *ibid.*, 740; *A.*, i, 475.

[74] " Special Report Series of the Medical Research Council," No. 61; H.M. Stationery Office, 1921.

for some hours at 120°, loses both its growth-promoting and its anti-rachitic power. Cod-liver oil is particularly active in both directions. Recently a number of papers have appeared on rickets in rats, which have been found suitable for this as well as for many other experiments on vitamins. A. F. Hess, G. F. McCann, and A. M. Pappenheimer[75] disagreed with Mellanby's view that a deficiency of fat-soluble vitamin is a cause of rickets, but McCollum and his co-workers have confirmed the effect of cod-liver oil in stimulating calcification processes after the production of rickets by defective diets. E. V. McCollum, N. Simmonds, P. G. Shipley, and E. A. Park[76] give a more complicated explanation of the causation of rickets. According to them, rickets (in rats) is not simply due to a deficiency of vitamin-*A*, as suggested (for dogs) by Mellanby. To produce rickets, the calcium : phosphorus ratio of the diet must be upset as well, making its calcium content relatively high, its phosphorus content low. With a calcium : phosphorus ratio differing from the optimal for normal ossification, rickets may still be avoided by giving an anti-rachitic substance. The ratio of calcium : phosphorus is considered by these authors to be of " infinitely greater importance " in ensuring normal ossification than the absolute amounts of these elements in the diet. The importance of calcium, as well as of vitamin-*A*, may perhaps to some extent reconcile the contradictory results of Mellanby and of Hess and his associates. Rather similar views were stated quite recently by V. Korenchevsky,[77] who concludes that a deficiency of calcium alone may affect the skeleton of rats in a manner suggestive of rickets, and that a deficiency of vitamin-*A* alone may also produce slight rickets; the changes typical of rickets are, however, most readily produced when the diet is deficient in both calcium and vitamin.

Thus a curious and novel relationship between vitamin-*A* and calcium metabolism is indicated. The latter is evidently of a complicated nature. P. Rona and D. Takahashi[78] showed ten years ago, by the method of compensatory dialysis, that 30—40 per cent. of the calcium in serum is non-diffusible, and last year A. R. Cushny[79] found that when serum is filtered through collodion all the crystalloids pass through, with the exception of some calcium and probably some magnesium. During rickets, there is a slight diminution in the calcium content of serum, during tetany after removal of the parathyroids there is a larger fall, but in either case this is at the expense of the diffusible portion; the

[75] *J. Biol. Chem.*, 1921, **47**, 395; *A.*, i, 757.

[76] *Ibid.*, 507; *A.*, i, 757.   [77] *Brit. Med. J.*, 1921, ii, 547.

[78] *Biochem. Z.*, 1911, **31**, 336; *A.*, 1911, ii, 302.

[79] *Ann. Reports*, 1920, **17**, 161.

non-diffusible calcium remains constant, according to L. von Meysenbug and G. F. McCann.[80] The calcium (and phosphorus) metabolism may also be disturbed, according to S. V. Telfer,[81] by the complete exclusion of bile from the gut, which brings in its train non-absorption of fatty acids and their excretion as calcium soaps in the fæces. The phosphoric acid, normally excreted as calcium salt by the intestine, is now eliminated in the urine.

Apart from metabolic questions, the mechanism of the deposition of calcium in the bones probably has a bearing on rickets. E. Freudenberg and P. György [82] have attempted to supply a (physico-chemical ?) basis for calcification. They conclude that cartilage takes up calcium from a $0.01N$-solution until an equilibrium is reached. Tryptic digestion and autolysis, as well as urea and ammonium chloride, inhibit calcium fixation. The authors suggest that normally the organism satisfies the conditions necessary for calcification, except where the process is inhibited by metabolites.

Chemotherapy.

Towards the end of 1920 an advance in chemotherapy became known, which promises to provide a cure for sleeping sickness and to rival the discovery of salvarsan, at least in scientific interest. L. Haendel and K. W. Joetten [83] report on a new trypanocide of great activity, which is referred to as " 205 Bayer." In a foot-note the editor of the journal states that he has exceptionally departed from the principle that no account could be taken of secret remedies, for the composition of the substance is not published, " in consequence of the judicially uncertain and unprotected position of German industry with respect to the former enemy countries." (An allusion to their treatment of German patents.) The authors, working in the Reichs-gesundheitsamt at Berlin, investigated a substance prepared by the Farbenfabriken vorm. Friedr. Bayer & Co., which frees mice, apparently permanently, from Nagana and other pathogenic trypanosomes in doses of 1/20 mg., and is lethal to the host only in doses of about 2 mg., or 40 times as much. The substance is rather specific, for spiro-chætes and the non-pathogenic *Trypanosoma Lewisii* are not much affected. M. Mayer and H. Zeiss [84] have published a more extensive investigation of the same substance, and place the subcutaneous

[80] *J. Biol. Chem.*, 1921, **47**, 541; *A.*, i, 754.
[81] *Biochem. J.*, 1921, **15**, 347; *A.*, i, 700.
[82] *Biochem. Z.*, 1921, **121**, 142.
[83] *Berl. Klin. Wochenschr.*, 1920, **57**, ii, 821; *A.*, i, 908.
[84] *Arch. Schiffs u. Tropenhygiene*, 1920, **24**, 257; *A.*, i, 908.

curative dose for mice at 0·06 mg. for *T. brucei* (Nagana), *T. equinum*, *T. equiperdum* (dourine), *T. gambiense* (human sleeping sickness), and *T. rhodesiense*, and the lethal dose at 10 mg., giving the extremely favourable ratio of 1 : 160. The substance does not kill the trypanosomes very rapidly, like potassium antimonyl tartrate, but takes about forty-eight hours to sterilise the host, apparently by stopping the reproduction of the parasite, of which undivided twin specimens are found in large numbers in the blood. Rats, guinea-pigs, and rabbits can also be cured permanently, and very favourable results have been obtained in natural dourine of horses. C. M. Wenyon [85] has quite recently confirmed these results for mice and *T. equiperdum* by intravenous injection. In view of the high ratio of lethal dose : curative dose, he observes that for sodium antimonyl tartrate in mice it is only 4. (For man it is <1, so that no cure with antimony can be effected.)

Although the exact composition of " 205 Bayer " remains a secret, the curiosity of chemists may perhaps to some extent be satisfied by a perusal of the patents of the years 1914—1916. Farbenfabriken vorm. Friedr. Bayer & Co.[86] describe the preparation of carbamides of the naphthalene series which are stated to be strongly trypanocidal. By the action of *p*-nitrobenzoyl chloride on 8-amino-α-naphthol-3 : 5- and -3 : 6-disulphonic acids (*K* and *H* acids), a compound results which, after reduction of its nitro-group, is condensed with carbonyl chloride to a complex carbamide, for instance,

OH NH·CO⟨ ⟩NH·CO·NH⟨ ⟩CO·NH OH

HO₃S⟨ ⟩ ⟨ ⟩SO₃H

SO₃H   SO₃H
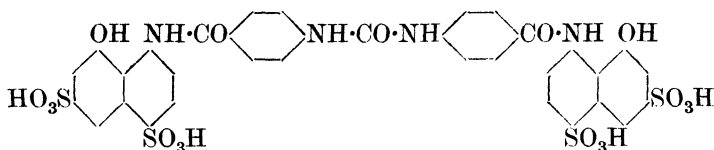
Instead of condensing with carbonyl chloride, the first condensation product may be united with a second molecule of *p*-nitrobenzoyl chloride and reduced, furnishing, for instance, for the 3 : 6-disulphonic acid the substance

OH NH·CO⟨ ⟩NH·CO⟨ ⟩NH₂

HO₃S⟨ ⟩SO₃H
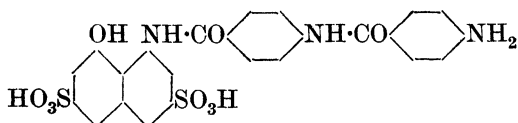
[85] *Brit. Med. J.*, 1921, ii, 746; *A.*, i, 908.

[86] D.R.-P. 278122; *Chem. Zentr.*, 1914, ii, 964; Brit. Pat. 9472 of 1914; *A.*, 1915, i, 14. See also D.R.-P.P. 289163, 289270—289272; *A.*, 1916, i, 390; Brit. Pat. 8591 of 1916; *A.*, 1918, i, 113; and further D.R.-P.P. 284938, 288272, 288273, 289107, and 291351.

and this may, in its turn, be converted into a carbamide sulphonic acid, which is used as the neutral sodium salt. Later patents indicate numerous substances with different substituents in the naphthalene and benzene rings, and the last one mentions a *m*-aminobenzoyl derivative of *m*-aminobenzoylaminosulphosalicylic acid, without any naphthalene ring. It will be seen that all these
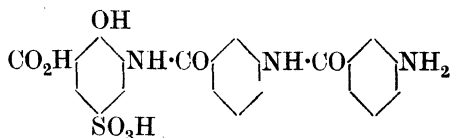
compounds, like polypeptides, contain several times the grouping NH·CO. They are dyes and resemble Trypanrot in being derivatives of naphthylaminesulphonic acids.

"Bayer 205" is very active on trypanosomes, but much less so on spirochætes; the reverse is the case with sodium bismuth tartrate, a new therapeutic agent recently introduced in France by R. Sazerac and C. Levaditi.[87] This analogue of tartar emetic is injected, suspended in oil, and has given very promising results in the treatment of human syphilis, but is not very effective against the Nagana trypanosome. Sodium antimonyl tartrate has of late years been found to be a specific against Kala-azar, due to a protozoon, and against the worm *Filaria sanguinis hominis*, but the administration of antimony in sleeping sickness has not been quite successful. There is at present some falling off in attempts to synthesise arsenic compounds which might rival salvarsan or its immediate derivatives, but our knowledge concerning the latter substance and its technical impurities is increasing. The biological testing of salvarsan has revealed the considerable variation in the toxicity of commercial samples and one of the reasons for this variation seems to be the use of sodium hyposulphite as a reducing agent. R. G. Fargher and F. L. Pyman[88] found that the slight sulphur content of technical preparations is due to admixture with a substance containing sulphur which enters the molecule in the reduction of 3-nitro-4-hydroxyphenylarsinic acid by sodium hyposulphite; with hypophosphorous acid this introduction may be avoided. W. G. Christiansen[89] has confirmed these results and states that the product prepared by hypophosphorous acid is relatively non-toxic. H. King[90] has now identified sulphur compounds which were regularly formed under the conditions employed by him in the reduction, to the

[87] *Compt. rend.*, 1921, **172**, 1391; **173**, 338; L. Fournier and L. Guénot, *ibid.*, 1921, **173**, 674; *A.*, i, 908.　　　　[88] *T.*, 1920, **117**, 373.
[89] *J. Amer. Chem. Soc.*, 1920, **42**, 2402.　　　　[90] *T.*, 1921, **119**, 1107.

extent of about 10 per cent.; this amount is large enough to account for all the sulphur of most specimens. These compounds are 3-amino-4-hydroxy-5-sulphinophenylarsinic acid, and (to a smaller extent) the corresponding arseno-derivative,

$$ OH{\Large<}{\Large>}AsO_3H_2 \qquad OH{\Large<}{\Large>}As\!:\!As{\Large<}{\Large>}OH \quad . $$

$$ \overset{NH_2}{\underset{SO_2H}{}} \qquad \overset{NH_2}{\underset{SO_2H}{}} \quad \overset{NH_2}{\underset{SO_2H}{}} $$
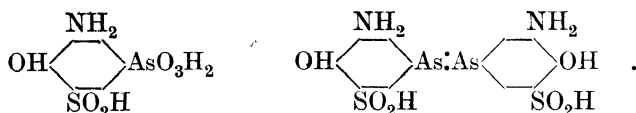
The latter is found to be twice as toxic to mice as salvarsan prepared by hypophosphorous acid.

Artificial Sweetening Agents.

Apart from saccharin, the only artificial sweetening agent which has met with practical application is dulcin, $EtO \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$. In the case of both substances, even the slightest modifications in the molecule generally abolish the sweet taste entirely. Thoms and Nettesheim [91] find that the methoxy-compound corresponding with dulcin is somewhat sweet, and the hydroxy-compound only very slightly so; all other derivatives had no sweet taste at all.

Pure saccharin, the more powerful of the two, is generally stated to be 550 times as sweet as sucrose, but Th. Paul [92] has shown that the comparison of sweetening powers is no simple matter. Saccharin and dulcin mutually reinforce one another; this pharmacological effect has been alleged to occur with a number of drugs and is well established in the case of opium alkaloids, for instance. As an example, Paul mentions that when 280 mg. of saccharin and 120 mg. of dulcin are dissolved in 1 litre of water, they cause the same sweetness as 535 mg. of saccharin by itself. A further complication [93] is that at various concentrations of the solution the ratio of the sweetening power of saccharin to sucrose is not constant and may vary from 200 in concentrated solution to 700 in dilute solution. Similarly, the ratio for dulcin varies from 70 to 350. In other words, both these substances are relatively sweeter in dilute solution. This phenomenon is not shown by the various sugars, which have a constant ratio of sweetness, independent of the concentration. The physiological effect of these synthetic substances is apparently of a different nature from that of the sugars.

A third artificial sweetening agent has lately become the subject of a patent [94] in which it is claimed that it is two thousand times as

[91] *Ber. deutsch. Pharm. Ges.*, 1920, **227**, 295.
[92] *Chem. Ztg.*, 1921, **45**, 38; *A.*, i, 109.
[93] *Ibid.*, 705. [94] S. Furukawa, Jap. Pat. 35332; *A.*, 1920, i, 676.

sweet as sucrose, so that it would be the sweetest substance known.. This is the α-*anti*-aldoxime of perillaldehyde; it has been further described by S. Furukawa and Z. Tomizawa.[95] Perillaldehyde,. $C_9H_{13} \cdot CHO$, is a lævorotatory liquid, b. p. 104°/9 mm., of unknown constitution, which forms 44—57 per cent. of the essential oil of the leaves of *Perilla nankinensis* Dcne., a Labiate known in Japan as " Shiso." The leaves are used as a vegetable or condiment. The oil of *P. ocymoides*, L., is a technical product in Eastern Asia (Wehmer, " Die Pflanzenstoffe," p. 822). According to Furukawa and Tomizawa, the *anti*-aldoxime of perillaldehyde, two thousand times as sweet as sucrose and four to eight times as sweet as saccharin, differs in this respect entirely from the β-*syn*-aldoxime, which is not sweet at all. These two substances therefore provide a novel and interesting example of the different physiological behaviour of stereoisomerides which has so far been principally studied in enantiomorphs (adrenaline, hyoscyamine, hyoscine). Perillonitrile, $C_9H_{13} \cdot CN$, is half as sweet as saccharin. It is a curious fact that the *anti*-oxime of perillaldehyde was described as long ago as 1910,[96] but that its sweet taste, now the reason for a patent, was not then noticed. Possibly organic chemists should more frequently taste their new compounds than they do at present.

GEORGE BARGER.

[95] *J. Chem. Ind. Tokyo*, 1920, **23**, 342; *A.*, 1920, i, 751.

[96] Schimmel & Co., *Bericht*, October, 1910; *A.*, 1910, i, 759.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

THE investigations in the past year have in the main followed the lines of previous years : there ,are, however, signs of more movement. In France, the *Annales de la Science Agronomique* has been restarted, under the able editorship of M. Albert Bruno, and already there is an increase in the output of scientific work. In England and in America, investigations begun after the Armistice are reaching the stage of publication, and certain directions of specialisation can now be observed. These will be indicated under the various headings.

Soil Investigations.

British soil investigators are studying the biological factors; American workers are ascertaining the properties and relationships of the soil solution and of the soil acidity; whilst Continental workers are studying the physico-chemical relationships of the soil. This course is economical of time and effort, but it would be attended by grave disadvantages if the specialisation proceeded so far as to obscure the fact that all three aspects of the subject are of vital importance to the study of soil fertility.

The Soil Solution.

The soil retains by absorption and surface attractions some 10 to 20 per cent. of its weight of water, distributed as films over its particles. The water dissolves some of the soil constituents, forming a solution which is of obvious importance as the medium through which plants and micro-organisms derive their food; indeed it may be regarded as the culture solution for the plant. Experimental work, however, is hampered by the difficulty of separating it from the soil; when soil contains moisture in percentages suitable for plant growth, the solution is held by the soil particles with such force that no ordinary means will remove it.

Various methods have been suggested for isolating the solution from the soil. Reasons are advanced 'for supposing [1] that the

[1] F. W. Parker, *Soil Sci.*, 1921, **12**, 209; *A.*, i, 914.

solution obtained by Ischerekov's displacement method [2] gives a more faithful representation of the soil solution than the other methods which have been used; ethyl alcohol was the best of the displacing fluids tested, and was without observed influence on the composition of the soil solution; successive portions of the displaced solution gave the same freezing-point depression and contained the same amount of total solids whilst the concentration was inversely proportional to the moisture of the soil.

It is, however, difficult to extract the solution, and methods have been devised for studying it in situ. It is suggested [3] that a study of the vapour pressure of the soil would give much valuable information, whilst the depression of the freezing point has been much studied by Bouyoucos in America. Hoagland and his colleagues [4] show that the latter method leads to substantially the same conclusions as the 1 : 5-water extraction method used in the United States.[5]

The water extract has not quite the same composition as the soil solution, but is not greatly dissimilar. When concentrated to have the same freezing point, it presumably resembles the actual solution also in concentration and should then undergo no change when placed in contact with soil. Experiment showed that this was the case, and probably for the first time in history a solution was poured through the soil and came out unchanged in composition.

The relationship between the concentration of the soil solution and plant growth has previously been studied in the case of barley; [6] similar results have now been obtained with maize, horse beans, potatoes, and turnips.[7] The concentration at any point in the soil is not significantly reduced until the plant root actually reaches it, that is, there is no drift of solutes in the soil apart from the movement due to drainage.

Apparently, however, the fact that a substance occurs in the soil extract affords no certain proof that it can be absorbed by plants. Orthoclase yields up potassium to water, but the dissolved potassium was not absorbable by wheat. It became available, however, when the solutions were treated with a mixture of hydrochloric and nitric acids.[8] Apparently the solute complex is not dissociated, and the plant is unable to take up the undissociated material.

[2] *Zhur. Opuitn. Agron.*, 1907, **8**, 147.

[3] M. D. Thomas, *Soil Sci.*, 1921, **11**, 409.

[4] D. R. Hoagland, J. C. Martin, and G. R. Stewart, *J. Agric. Res.*, 1920, **20**, 381; *A.*, i, 214.

[5] G. R. Stewart, *ibid.*, 1918, **12**, 311.

[6] *Ann. Reports*, 1918, **15**, 173; 1919, **16**, 172.

[7] G. R. Stewart and J. C. Martin, *J. Agric. Res.*, 1921, **20**, 663.

[8] J. F. Breazeale and L. J. Briggs, *ibid.*, 615; *A.*, i, 388.

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The variation in composition of soil solution brought about by plant growth affects the degree of dispersion of the colloidal material of the soil; a large increase in dispersion was observed when the soil solution was depleted as the result of absorption of solutes by the plant.[9]

The same change has been studied in a different manner in Germany, where Wiegner's method has been successfully used by von Seelhorst to study the changes in physical condition of soil brought about by cropping and manuring.[10]

There is a constant interchange between the colloids of the soil and the soil solution, and the ions affect the state of coagulation of the colloids.[11]

Soil Constituents.

The soil constituents fall into two great groups—organic substances which have been synthesised in the growing plant and then returned to the soil either directly or through the bodies of animals or micro-organisms, and inorganic substances derived from the minerals in the soil, which very often have also passed into plants and been liberated on the decay of the leaves, stems, or roots. Among the organic constituents, one of the most interesting is humus, a black, sticky substance to which important properties have been attributed, although it must be admitted that the direct evidence is not very strong. Two views have been put forward as to its origin. Beckley [12] supposes that the carbohydrates decompose to form hydroxymethylfurfuraldehyde, which then condenses to form humus; some experimental evidence is given for this view, which has also been put forward independently.[13] Eller and Koch,[14] on the other hand, suppose that humus is formed by oxidation of quinones which arise by the elimination of water from hexoses. They assign to it the formula $C_6H_4O_3$:
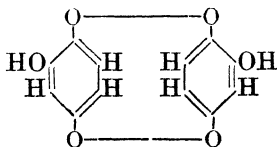
[9] D. R. Hoagland and J. C. Martin, *J. Agric. Res.*, 1920, **20**, 397; *A.*, i, 215.

[10] C. von Seelhorst, W. Geilmann, and H. Hubenthal, *J. Landw.*, 1921, **69**, 5; W. Geilmann and A. von Hauten, *ibid.*, 105.

[11] L. Casale, *Staz. sperim. agrar. ital.*, 1921, **54**, 65.

[12] V. A. Beckley, *J. Agric. Sci.*, 1921, **11**, 69; *A.*, i, 227.

[13] J. Marcusson, *Ber.*, 1921, **54**, [*B*], 542; *A.* i, 313.

[14] *Ibid.*, 1920, **53**, [*B*], 1469; *A.*, 1920, i, 733. See also W. Eller, *Brennstoff-Chem.*, 1921, **2**, 129; *A.*, i, 506; H. Stoltzenberg and M. Stoltzenberg-Bergius, *Z. physiol. Chem.*, 1920, **111**, 1; *A.*, i, 32.

Against this view it is urged [15] that natural humus, unlike benzene derivatives, cannot be sulphonated or nitrated, whilst other experiments indicate that the acidity is due to carboxyl and not to phenolic groups.[16]

Several interesting papers have appeared on clay, using the word in the sense of the soil investigator, and not of the ceramic chemist. This is the fraction of soil the particles of which are 0·002 mm. or less in diameter. This has been subdivided into twenty-six fractions by elutriation methods and each fraction fully analysed. About 80 per cent. of the total clay had a fairly constant composition, closely approximating to the theoretical clay complex, $Al_2O_3,2SiO_2,2H_2O$. The remaining fractions, consisting of the coarser grades, showed a gradually increasing silica content.[17]

A suggestive investigation which recalls some earlier work by Schloesing père has been published from the United States Bureau of Soils.[18] Aqueous extracts of soil frequently contain a considerable amount of colloidal material, which renders them opalescent even after standing, and no ordinary filtration suffices to clear them. Quantities of this material have been extracted from soil and examined; it consists mainly of hydrated silicate of aluminium with varying amounts of ferric hydroxide, silicic acid, organic matter, and possibly aluminium hydroxide, with small amounts of calcium, magnesium, potassium, and sodium. It showed marked colloidal properties and to it is attributed much of the colloidal characteristics of the soil. Its power of absorbing gaseous ammonia and dyestuffs was investigated, and on this is based a method for estimating the amount present in soils; in the case examined, this was 28 per cent., the clay on the American basis (0·005 mm. diameter) being 35·9 per cent. The material is called " ultra-clay "; it may be substantially the same as " clay " in the British sense (0·002 mm. diameter).

Soil Acidity.

Many soils are greatly improved by the addition of lime, and the obvious explanation is commonly put forward that they have in some way become acid and therefore infertile, but that fertility is restored on neutralisation. The explanation was seriously called in question when it was shown that absorption would account for many of the observed facts, and the tendency in recent years has been to analyse the phenomena more closely.[19]

[15] J. Marcusson, *loc. cit.*; *Z. angew. Chem.*, 1921, **34**, 437; *A.*, ii, 590.

[16] Sven Odén, *Koll. Chem. Beihefte*, 1919, **11**, 75; *A.*, i, 393.

[17] E. Blanck and F. Preiss, *J. Landw.*, 1921, **49**, 73.

[18] C. J. Moore, W. H. Fry, and H. E. Middleton, *J. Ind. Eng. Chem.*, 1921, **13**, 527.

[19] For critical discussion, see E. A. Fisher, *J. Agric. Sci.*, 1921, **11**, 19; *A.*, i, 215; A. Demolon, *Ann. Sci. Agron.*, 1920, **37**, 97.

An acid filtrate is obtained when a solution of a neutral salt is poured through the soil. In the case of potassium nitrate and sodium chloride, this has been traced to aluminium and iron rendered soluble by basic exchange; whilst in the case of calcium acetate and potassium acetate it is due to acetic acid liberated either by replacement of the hydrogen of hydrous silicates or by selective absorption of the basic element in the salt solution.[20]

Other causes of acidity have been investigated. It is not clear, however, that the true acidity as measured by hydrogen-ion concentration is ever sufficient in nature greatly to affect the growth of plants. It is easy to be misled by the results of laboratory experiments. Degrees of acidity which proved inhibitive to micro-organisms such as *Azotobacter* and *Actinomycetes* had no observable effect on the growth of wheat in culture solutions.[21] Moreover, crops grown in sand cultures showed a higher degree of tolerance of acidity than those grown in culture solutions.[22] Indeed, sand cultures containing solutions of P_H [23] value 3 and therefore acid gave better growth than those more nearly neutral. In the latter case, however, the plants were chlorotic, and it is possible that the results are due to lack of available iron. Natural soils present even more complexity, since they show a high degree of buffering, which coarse sand does not.[24]

Meanwhile, however, results are being accumulated and the question of method is important. The colorimetric method for determination of P_H values is so much more rapid than the electrometric method that it would be universally adopted if it were equally trustworthy. A careful examination has revealed [25] some of its defects and has emphasised the effect of fineness of division of the soil.

Methods of controlling the soil reaction are also being worked out. It is suggested [26] that addition of sulphur to soil might produce acidity which would be useful in checking the potato scab organism (*Actinomyces chromogenus*, Gasperini). Good field results are recorded, especially where the organism that oxidises the sulphur is added; the yield of potatoes was increased by 50 per cent., whilst the percentage of unsaleable scabby potatoes fell from 58 to 29 per cent. of the total crop.[27]

[20] R. H. Robinson, *Soil Sci.*, 1921, **11**, 353; *A.*, i, 644. See also J. J. Mirasol, *ibid.*, 1920, **10**, 153; *A.*, i, 88.

[21] H. F. A. Meier and C. F. Halstead, *ibid.*, 1921, **11**, 325.

[22] A. G. McColl and J. R. Haag, *ibid.*, 1921, **12**, 69.

[23] P_H is the expression used for $-\log[H^{\cdot}]$.

[24] R. E. Stephenson, *Soil Sci.*, 1921, **12**, 145.

[25] E. A. Fisher, *J. Agric. Sci.*, 1921, **11**, 45.

[26] J. G. Lipman, A. L. Prince, and W. A. Blair, *Soil Sci.*, 1921, **12**, 197.

[27] W. H. Martin, *ibid.*, 1921, **11**, 75; see also J. G. Lipman, A. W. Blair, W. H. Martin, and C. S. Beckwith, *ibid.*, **11**, 87.

Another direction for utilising the acidity produced by addition of sulphur to soil is in removing the last of the alkalinity from alkali soils after most of the salts have been washed out by irrigation water.[28]

The converse problem of reducing acidity by addition of lime or of calcium carbonate has been studied. The relationship between added calcium hydroxide and P_H value (as measured by electrometric titration) is not simple,[29] and some of the acid soils, for example, in Oregon, do not respond to lime treatment.[30] No explanation is forthcoming and further work is called for. Moreover, it appears that soils contain not only calcium but magnesium carbonate also, and these do not behave alike.[31]

In general, however, acidity is rectified by addition of calcium carbonate, and from the practical point of view it is desirable to have some method that will show how much must be added to soil to ensure a neutral reaction. The Hutchinson-McLennan method is shown to give useful indications.[32] In addition to calcium carbonate, other materials can be used; experiments are recorded with a slag described as " dicalcium silicate." [33]

Soil problems, however, are very complex and lime must not be regarded solely as a neutralising agent. Reference has already been made to the chlorosis induced in sand cultures when neutrality was ·maintained. Other observations indicate that the chlorosis induced by lime in calcareous soils is due to depression in the availability of iron. Evidence from ash analysis of chlorotic plants seems to point to lack of iron as one cause of the chlorosis, a possible contributory cause being excess of lime (see p. 208). Rice became chlorotic in calcareous soils with ordinary percentages of water, but it made normal healthy growth when the soil was submerged. It is suggested that special roots are formed under submerged conditions better able to assimilate iron than the ordinary root.[34]

A further effect of lime, which is often harmful, is to influence the potash supply to the plant.[35] It appears that potassium assimilation by plants is adversely affected by lime when only small amounts of potassium are present. In practice, this particular difficulty can be overcome by supplying potassic fertilisers.

Further, the phosphate supply is affected by calcium carbonate.

[28] P. L. Hibbard, *Soil Sci.*, 1921, **11**, 385; J. L. Lipman, *ibid.*, 1916, **2**, 205.

[29] C. O. Swanson, W. L. Latshaw, and E. L. Tague, *J. Agric. Res.*, 1921, **20**, 855.

[30] R. H. Robinson and D. E. Bullis, *Soil Sci.*, 1921, **11**, 363; *A.*, i, 644.

[31] F. Hardy, *J. Agric. Sci.*, 1921, **11**, 1; *A.*, i, 215.

[32] Ch. Brioux, *Ann. Sci. Agron.*, 1920, **37**, 233.

[33] C. J. Schollenberger, *Soil Sci.*, 1921, **11**, 261.

[34] P. L. Gile and J. O. Carrero, *J. Agric. Res.*, 1920, **20**, 33.

[35] P. Ehrenberg, *Landw. Jahrb.*, 1919–20, **54**, 1.

The retention by soil of the P_2O_5 of superphosphate is regarded [36] as a chemical interaction if calcium carbonate is present, but as a physical adsorption if it is absent. In the former case dicalcium phosphate is formed so rapidly that the whole of the phosphate is precipitated within a very restricted range : this becomes slowly converted into tricalcium phosphate.

The physical adsorption in non-calcareous soils is rather different and less rapid, so that the phosphate washes further down into the soil. On non-calcareous soils, therefore, phosphatic manuring should be more effective than on calcareous soils.

As always happens in soil investigations, it is necessary to distinguish clearly between the phenomena observed in soils devoid of vegetation and those on which plants are growing. The former present the simpler case and are necessarily studied first; the plant introduces so much complication that even now little has been ascertained with certainty. The relationships between soil reaction and absorption of ions are complicated in presence of the growing plant by the circumstance that different plants vary in their power of absorbing nutrients from the soil : maize could absorb difficultly soluble phosphates from acid soils only; mustard could take it under more nearly neutral conditions.[37]

These various observations must not, however, be taken as indicating that acid soils are in general more favourable than neutral soils for the yielding up of nutrients to the plant. It is true that excess of calcium carbonate seems to be harmful in some cases, but there is also evidence that plants usually obtain phosphates more easily from neutral than from acid soils.[38]

Effect of Salts on Soil.

Just as lime has a complex action on soil so also do various salts. There is an exchange of bases [39] which may lead to an acid reaction, as already stated. There are also important physical effects arising out of the flocculation of clay by dissolved salts. These have been studied at Rostock in an important investigation by Nolte : [40] they have also received attention in America. In the American investigations, sodium salts cause clay to become harder and less permeable to water. This is objectionable in regions where irrigation is necessary, and in such cases the water must be examined to see if it

[36] W. H. Harrison and S. Das, *Pusa Memoirs Chem. Series*, 1921, **5**, No. 9.

[37] M. Wrangell, *Landw. Versuchs. Stat.*, 1920, **96**, 209.

[38] G. S. Fraps, *Texas Agric. Expt. Station Bull.*, 1920, 267; also O. M. Shedd, *Soil Sci.*, 1921, **11**, 111.

[39] For details, see W. P. Kelley and A. B. Cummins, *ibid.*, 1921, **11**, 139; *A.*, i, 388.

[40] O. Nolte, *J. Landw.*, 1919, **67**, 267.

contains more sodium and potassium than calcium and magnesium; if so, its continued use is likely to be harmful. The suggestion is made that addition of soluble calcium or aluminium compounds to the water might overcome the difficulty.[41]

Soil Analysis.

One of the most difficult problems for the agricultural chemist is that of soil analysis. He is expected to analyse soils and on the basis of his results to give recommendations as to manuring. Unfortunately, the problem is particularly difficult; in most cases insoluble on our present knowledge. The trouble arises from the fact that no two methods give the same results; it is possible from the Rothamsted soils to extract percentages of K_2O varying from 0·001 to 5 per cent., according as one extracts with water or adopts drastic fusion methods. Two important summaries and discussions of the German results [42] show the relative importance there attached to the various factors, and indicate high-pressure steam as a suitable agent in potash determinations. Another suggestion is that the ratio of soluble to total K_2O or P_2O_5 (using 1 per cent. citric acid as the agent for soluble P_2O_5 and 10 per cent. hydrochloric acid for soluble K_2O) is more useful than either figure taken separately in explaining fertiliser results. The authors carefully disclaim, however, any predictions of fertiliser requirements.[43] It is suggested also that the plant is able to extract from a soil more K_2O but less P_2O_5 than is dissolved by 1 per cent. citric acid.

The use of $0·2N$-nitric acid for soil analysis has been further discussed [44] and also that of hydrochloric acid.[45]

Mechanical analysis of soil,[46] at present a very tedious process, promises to be simplified by using sodium carbonate as the deflocculating agent instead of ammonia, whilst the use of the centrifuge still further accelerates the process.[47]

Finally, a promising attack has been made on the exceedingly difficult problem of determining the amount of colloidal material in soils.[48]

[41] C. S. Schofield and F. B. Headley, *J. Agric. Res.*, 1921, **21**, 265.

[42] J. König and J. Hasenbäumer, *Landw. Jahrb.*, 1920, **55**, 184; J. König, J. Hasenbäumer, O. Kleine-Möllhoff, and M. L. Plouski, *ibid.*, 1921, **56**, 439.

[43] O. Lemmermann, L. Fresenius, and H. Wiesmann, *Landw. Versuchs. Stat.*, 1921, **98**, 155.

[44] O. M. Shedd, *Soil Sci.*, 1921, **11**, 111.

[45] F. Munter, *Landw. Versuchs. Stat.*, 1919, **94**, 181.

[46] For a discussion of methods, see U. Pratolongo, *Ricerche R. Scuola Sup d'Agric. di Milano*, 1920, **6**, 97.

[47] A. F. Joseph and F. J. Martin, *J. Agric. Sci.*, 1921, **11**, 293.

[48] C. J. Moore, W. H. Fry, and H. E. Middleton, *J. Ind. Eng. Chem.*, 1921, **13**, 527; *A.*, ii, 608.

Environmental Conditions.

A detailed study of soil temperatures [49] brings out the interesting fact that the top 6 inches of soil is on the whole rather warmer than the air, so that the temperature conditions are more favourable to micro-organisms and plant roots than might be expected.

Water.

Soil water is generally divided into three forms—gravitational (the excess that can drain away), capillary (the free water held to the surface of the soil particles by capillary forces), and hygroscopic (water which is in equilibrium with the vapour of a saturated atmosphere). The division is convenient and intelligible. Bouyoucos, who has for several years studied the freezing of water in soil, substitutes [50] the following classification, which has the advantage of being more specific :

Gravitational. Unsuitable for plant growth.

Free. Freezing readily near 0° or just below (−1·5°). Readily available for plants.

Unfree ⎰ Not freezing until −4° or lower. Capillary adsorbed; only very slightly available for plant growth.

Not freezing at −78°. Combined : either water of hydration or water of solid solution; unavailable for plants.

According to this scheme, the wilting point corresponds closely with the water that fails to freeze at −1·5°, that is, the unfree water. He claims [51] that the amount of " unfree " water in the soil is a constant, not, as Keen supposed, a function of the total water.

He further argues [52] that the solution around the soil particles and in the very fine capillary spaces is less concentrated than the mass of the soil solution; this is, of course, against the current conventions.

The physical principles involved in the distribution of water in the soil have been discussed by Wilsdon,[53] whilst an admirable account has appeared of the relationship of clay to the adsorption of water.[54]

The water supply of the soil affects not only the rate of growth of the plant, but also to some extent its composition. The concen-

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[49] B. A. Keen and E. J. Russell, *J. Agric. Sci.*, 1924, **11**, 211.
[50] G. Bouyoucos, *Soil Sci.*, 1921, **11**, 33.
[51] *Ibid.*, 255.   [52] *Ibid.*, 131.
[53] B. H. Wilsdon, *Pusa Memoirs, Chemical Series*, 1921, **6**, No. 3.
[54] Sven Odén, *Trans. Faraday Soc.*, 1921, **17**, 244.

tration of cell sap has been shown to depend on the moisture content of the soil; apparently this is the chief factor concerned. A low concentration (induced by high moisture content) is associated with rapid vegetative growth; a high concentration with slower growth but with fruit bud formation.[55]

Soil Organisms.

The relationships existing between the growing plant and the micro-organic population of the soil are gradually being elucidated,[56] but the papers published this year deal largely with matters of detail. The range of substances decomposable in the soil by micro-organisms is remarkable, and includes some of the very stable hydrocarbons such as paraffins, benzene, toluene, etc.; [57] it is even suggested that soil organisms could be used in gas analysis for discriminating between certain hydrocarbons.

Most of the investigations, however, deal with the nitrogen cycle. Many organisms are capable of decomposing protein with formation of ammonia; it is not usual to discriminate between these in soil investigations, but only to count them; a comparison has been made of different counting methods adopted.[58]

In nature, the ammonia is almost invariably oxidised bacterially to nitrate, and attempts have several times been made in France to utilise this action on the manufacturing scale : a new method is suggested in which ammonium salts percolate through peat or volcanic scoriæ.[59]

The bacterial fixation of nitrogen continually attracts attention : it is effected by two groups of organisms, *Azotobacter* and *Clostridium*. The former is usually regarded as the more important; it assimilates nitrogen more slowly at ordinary laboratory temperature than at 27°, but fixes more per unit of mannite consumed.[60] The effects of coloured light and of uranium salts have also been studied. A method of estimating the numbers of *Clostridium* in the soil has been devised,[61] and the view is put forward that it is more numerous than *Azotobacter* and probably plays a more important part in the fixation of nitrogen.

[55] H. S. Reed, *J. Agric. Res.*, 1921, **21**, 81.

[56] For a recent summary, see E. J. Russell, *Ann. Sci. Agron.*, 1921, **38**, 49.

[57] J. Tausz and M. Peter, *Centr. Bakt. Par.*, 1919, [ii], **49**, 497; *A.*, 1920, i, 911.

[58] Z. N. Wyant, *Soil Sci.*, 1921, **11**, 295.

[59] E. Boullanger, *Ann. Inst. Pasteur*, 1921, **35**, 575; *A.*, i, 836.

[60] E. Kayser, *Compt. rend.*, 1920, **171**, 969; *A.*, i, 79; *ibid.*, 1921, **172**, 183, 493, 939, 1133; *A.*, i, 208, 479.

[61] G. Truffaut and N. Bezssonoff, *ibid.*, 1921, **172**, 1319.

A third group of organisms acts in symbiosis with leguminous plants and is closely related in activity to the growth of the plant.[62] Morphologically they present many features of interest.[63]

Other organisms seem concerned in the loss of nitrogen from soil, some of which is presumably brought about by an evolution of gaseous nitrogen. Although little is known of the mechanism of the process, further measurements have been made of the quantities involved. In the New Jersey cylinder experiments, which extended over a period of twenty years,[64] the loss has usually been of the order of 100 lb. per acre for the first fifteen years; where, however, green manure was used, there was no loss, but a gain.

Partial Sterilisation.

Further results have been published [65] showing the increase of crop yield resulting from heat treatment of soil. The effects persisted for several crops; they varied somewhat, however, with the different layers of soil. The introduction of untreated soil did not wholly counteract the effect of steaming, showing that the decomposition of soil materials is a potent factor in determining the effect.

Owing to the cost and limited application of heat, efforts are continued to find some chemical agent capable of modifying the soil population in the desired direction. Studies have been made of *p*-dichlorobenzene, which gave promising results against the Peach-tree Borer (*Sanninoidea exitiosa*, Say), a destructive pest of peach trees,[66] and of the physical and other conditions affecting the use of carbon disulphide as a soil sterilising agent.[67]

Phenol has also proved effective, but it is liable to certain obscure interactions with soil constituents and to biochemical decomposition in the soil whereby its value is much diminished.[68]

Chloropicrin and formaldehyde are useful partial sterilising agents,[69] and their effect on germination has been discussed.[70]

[62] A. L. Whiting and W. R. Schoonover, *Soil Sci.*, 1920, **10**, 441.

[63] F. Löhnis and R. Hansen, *J. Agric. Res.*, 1921, **20**, 543.

[64] J. G. Lipman and A. W. Blair, *Soil Sci.*, 1921, **12**, 1.

[65] Viscount Elveden, *J. Agric. Sci.*, 1921, **11**, 197.

[66] A. Peterson, *Soil Sci.*, 1921, **11**, 305.

[67] B. R. Leach, *ibid.*, 1921, **10**, 421.

[68] N. N. Sen Gupta, *J. Agric. Sci.*, 1921, **11**, 136.

[69] E. J. Russell, *J. Roy. Hort. Soc.*, 1920, **45**, 237.

[70] E. Miège, *Compt. rend.*, 1921, **172**, 170 (chloropicrin); A. H. Hurd, *J. Agric. Res.*, 1920, **20**, 209 (formaldehyde).

The Chemistry of the Living Plant.

Photosynthesis.

The rapid production of sugar in the leaf from carbon dioxide continues to evoke a great volume of research. Baeyers' original hypothesis still holds the field, and there is no generally recognised alternative to the view that the first product is formaldehyde, which subsequently condenses to sugar. The key-sugar in carbon metabolism, both in the up- and the down-grade processes, appears to be glucose. The pentoses, however, are invariably present and play an important part in plant processes, entering into the composition of the nucleus, of certain cell-walls and of mucilage,[71] and helping considerably in determining succulence.[72]

Numerous investigations have shown that formaldehyde is obtainable in circumstances more or less comparable with those obtaining in natural photosynthesis. The more notable papers include one from a physico-chemical laboratory where the chemical pitfalls are avoided,[73] and one from a physiological laboratory where the plant conditions are fully recognised.[74] In the latter it is claimed that the production of formaldehyde results from the decomposition of ·chlorophyll and is not directly dependent on the presence of carbon dioxide. An interesting discussion, which, moreover, invites controversy, is contained in the Hugo Müller lecture.[75] An alternative view is put forward by Mazé in which the principal part is assigned to hydroxylamine. This base is supposed to arise in the leaves by reduction of nitric acid (nitrates being the recognised nitrogenous nutrients of plants and absorbed in considerable quantities from the soil); it combines with carbon dioxide and changes as follows :

$$CO_2,NH_2 \cdot OH = H \cdot CHO + HNO_2,$$
also
$$2CO_2,NH_2 \cdot OH = CH_2(OH) \cdot CHO + 2HNO_2.$$
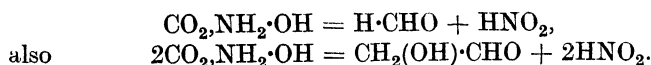
These products are actually found in the leaves of the elder. The glycollaldehyde may become reduced to acetaldehyde; this reacts to produce lactaldehyde and nitrous acid,

$$CH_3 \cdot CHO + CO_2,NH_2 \cdot OH = CH_3 \cdot CH(OH) \cdot CHO + HNO_2,$$
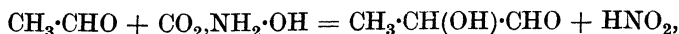
[71] F. F. Blackman, *New Phytologist*, 1921, **20**, 2.

[72] H. A. Spoehr, " The Carbohydrate Economy of the Cacti," Carnegie Inst. Pub. No. 287, 1919.

[73] E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *T.*, 1921, **119**, 1025.

[74] W. J. V. Osterhout, *Amer. J. Bot.*, 1918, **5**, 511; *A.*, i, 263.

[75] B. Moore, *T.*, 1921, **119**, 1555.

which occur in the leaves of the poplar. It is not difficult in this way to build up substances of any desired degree of elaboration.[76]

Whatever view is taken as to the actual course of photosynthesis, it is known that potassium plays an important part, although there is not necessarily a specific effect. It is shown that wheat can produce and translocate a certain amount of starch in presence of only little of this element.[77] It does not appear that the potassium is in organic combination in the plant, since it can all be extracted with water.[78]

Iron also has always been regarded as essential for the production of chlorophyll. It is now maintained that the magnesium salt of pyrrolecarboxylic acid serves instead, and in culture solutions determines the formation of chlorophyll even in absence of iron. It is therefore suggested that the function of iron in the leaf is to act as catalyst in the formation of pyrrole, which is regarded as the centre of the chlorophyll complex.[79]

Other inorganic nutrients are essential to plant growth, and special importance has always been attached to nitrogen, potassium, and phosphorus because of the striking results obtained by the use of their compounds as fertilisers. Attempts have been made to find quantitative relationships between the amounts of plant nutrients supplied and of the subsequent plant growth. The old idea that growth was proportional to the quantity of fertiliser had long ago to be abandoned; it was followed by Mitscherlich's view that the effect of a nutrient salt (or other factor) is proportional to the decrement from the maximum obtainable when that salt or factor is present in ample quantity. This view has the merit that it is readily expressible in the form of a logarithmic equation, the constants of which hold out attractive possibilities for the agricultural chemist; it has, however, evoked a storm of criticism in Germany,[80] and in any case it appears to be too simple a statement, as the results are more readily expressible by a sigmoid than by a logarithmic curve.[81]

[76] P. Mazé, *Compt. rend.*, 1921, **172**, 173; *A.*, i, 209. See also *ibid.*, 1920, **171**, 1391; *A.*, i, 151.

[77] T. O. Smith and O. Butler, *Ann. Bot.*, 1921, **138**, 189; *A.*, i, 482.

[78] S. Kostychef and P. Eliasberg, *Z. physiol. Chem.*, 1920, **111**, 228; *A.*, i, 83.

[79] B. Oddo and G. Polacci, *Gazzetta*, 1920, **50**, 54; *A.*, 1920, i, 407.

[80] Among recent papers are A. Mitscherlich, *Landw. Jahrb.*, 1921, **56**, 71; B. Baule, *ibid.*, 1920, **54**, 493; A. Mayer, *Landw. Versuchs. Stat.*, 1919, **94**, 247. For a useful résumé, see E. Lang, *Landw. Jahrb.*, 1920, **55**, 337.

[81] Rothamsted Report, 1918–20, p. 14; A. Rippel, *Landw. Versuchs. Stat.*, 1921, **97**, 357. For a discussion of the distinction between growth rate and final growth, see C. West, G. E. Briggs, and F. Kidd, *New Phytologist*, 1920, **19**, 200.

There has been much discussion, initiated by Shive and Totting-ham's earlier work, as to the need for some definite physiological balance between the various plant nutrients; it is, however, shown [82] that there is no " best" solution for plant growth: a considerable range of mixtures is possible, although " poor " solutions can be made.[83]

Some proportionality between CaO and MgO seems indicated by consideration of the analyses of plant ash.[84]   A detailed study of the potato in sand cultures is also reported.[85]

Further, it is possible to effect disturbances in plant nutrition by altering the course of absorption of the nutrients.   Assimilation becomes abnormal when a plant root is divided among several nutrient solutions from each of which one essential nutrient is withheld.   It is suggested that the cause lies not so much with the actual absorption of the nutrient as with the subsequent transloca-tion, and values have been calculated for nitrogen, phosphoric acid, and potassium which show a reasonable measure of agreement with the results actually found.[86]

The older agricultural chemists confined themselves almost exclusively to the three nutrients nitrogen, phosphorus, and potass-ium; of recent years, however, the French chemists have directed attention to the importance of other elements.   Bertrand first insisted on the importance of manganese and now shows [87] that it is invariably present, the supposed exceptions of Maumené being non-existent.   Copper is shown to be invariably present in plants; it is subject to translocation and migrates to points of greatest vitality as if it played an active part in intracellular metabolism.[88]

Iron presents a somewhat more complex problem, since it exists in the plant in two forms which are not readily distinguished : as Fe_2O_3 deposited by evaporation in the leaf or absorbed in the cellular membranes,[89] and as an organic complex comparable with Bunge's hæmatogen; the latter becomes translocated and moves towards the centres of active life and reproduction.[90]

[82] A. R. Davis, *Soil Sci.*, 1921, **11**, 1.

[83] Confirmed also by L. H. Jones and J. W. Shive, *J. Agric. Res.*, 1921, **21**, 701.

[84] H. Lagatu, *Compt. rend.*, 1921, **172**, 129; *A.*, i, 214.

[85] E. S. Johnston, *Soil Sci.*, 1920, **10**, 389.

[86] P. L. Gile and J. O. Carrero, *J. Agric. Res.*, 1921, **21**, 545.

[87] G. Bertrand and Mme M. Rosenblatt, *Compt. rend.*, 1921, **173**, 333; *A.*, i, 759; J. S. Jones and D. E. Bullis, *J. Ind. Eng. Chem.*, 1921, **13**, 524; *A.*, i, 840.   For a soil study, see P. Nottin, *Ann. Sci. Agron.*, 1920, **37**, 228.

[88] L. Maquenne and E. Demoussy, *Compt. rend.*, 1920, **170**, 87.   See also a suggestive paper by these authors in *Ann. Sci. Agron.*, 1921, **38**, 113.

[89] For this inorganic iron, see H. W. Jones, *Biochem. J.*, 1920, **14**, 654; *A.*, 1920, i, 909.

[90] L. Maquenne and R. Cerighelli, *Compt. rend.*, 1921, **173**, 273; *A.*, i, 759.

A study of iron nutrition has shown that the availability and sufficiency of a particular iron compound depends on the other constituents of the nutrient solution and on its hydrogen-ion concentration.[91] Thus ferric phosphate was of little value to plants when the nitrogenous nutrient was a nitrate; but it was quite effective when ammonium sulphate was used. On the other hand, ferrous sulphate was effective in presence of nitrates, but toxic when used in conjunction with ammonium sulphate.

Pot experiments suggest that small doses of boric acid cause an increase in plant growth, but it is not clear that crop increases are produced in the field. The subject is of some importance in America, because boron occurs in some of the naturally occurring potassium salts which have been proposed for use as fertiliser; it is found that 3 to 5 lb. per acre is the largest permissible dose of anhydrous borax, and there was no evidence of any beneficial effect with this or smaller quantities.[92]

It is probable that all these effects are complex. Finely powdered sulphur, when added to soil in certain cases, increases plant growth; the action is considered to include at least three factors; some of the sulphur is oxidised by bacteria to sulphuric acid, which brings into solution more phosphate, potassium, etc.; it seems to stimulate the activities of the ammonifying, the nitrifying, and the nodule organisms; and apparently [93] it stimulates the production of starch in plants.

Possibly some such action may explain the curious observation that beans germinated and grown in distilled water became etiolated and died for want of food, whilst large reserves still remained in the cotyledons. On the other hand, growth continued in soil and exhaustion of reserves was much more complete.[94]

Plant Constituents.

This branch of the subject belongs properly to organic chemistry, and only brief reference will be made to it here. The fundamental product is starch, but its transformations cannot be followed with certainty because no satisfactory method exists for its determination n plants. Taka-diastase converts it into maltose and dextrose only, and was therefore proposed [95] as a suitable analytical agent; it now appears,[96] however, that this substance does not give concordant

[91] L. R. Jones and J. W. Shive, *J. Agric. Res.*, 1921, **21**, 701; *Soil Sci.*, 1921, **11**, 93.

[92] J. R. Neller and W. J. Morse, *Soil Sci.*, 1921, **12**, 79.

[93] G. Nicolas, *Compt. rend.*, 1921, **172**, 85.

[94] G. D. Buckner, *J. Agric. Res.*, 1921, **20**, 875.

[95] W. A. Davis and A. J. Daish, *J. Agric. Sci.*, 1914, **6**, 152.

[96] E. Horton, *ibid.*, 1921, **11**, 240.

results, and indeed doubt is expressed whether any ordinary enzyme would do so. Until he can follow the more important changes in the growing plant, the agricultural chemist is not as a rule directly concerned with questions of constitution of these various constituents.[97]

The nitrogen compounds in plants are steadily being investigated. A method is suggested for extracting the protein from leaves by use of water saturated with ether.[98]

Nitrogen compounds have been extracted and examined from lucerne seed,[99] pecans, peanuts, and kafir,[1] mungbean[2] (*Phaseolus aureus*, Roxburgh), coconut[3] (*Cocus nucifera*), cohune nut (*Attalea Cohune*),[4] and the egg plant (*Solanum melongena*, L.).[5]

Some work has also been done on the formation of alkaloids.[6] Annett[7] has continued his studies of the morphine content of poppies and has made a survey showing the quantity of opium produced from this crop in the more important districts in India.

That most remarkable of all chemical processes, the synthesis of nitrogen compounds from gaseous nitrogen in the nodules on the clover root, has been further examined but not yet elucidated;[8] about 60 per cent. of the soluble nitrogen in the nodules of soy bean is precipitated by phosphotungstic acid; apparently, however, no globulin is present and only a small amount of albumin.[9] Field experiments show the great advantage of inoculation for soy beans, and on certain soils, for canning peas.[10]

[97] Among the papers are : " Starch," M. Samec and H. Haerdtl, *Koll. Chem. Beihefte*, 1920, **12**, 281; *A.*, i, 226; P. Karrer *et al.*, *Helv. Chim. Acta,* 1921, **4**, 678; *A.*, i, 768. " Cellulose," K. Hess, *Helv. Chim. Acta*, 1920, **3**, 866; *A.*, i, 12; P. Karrer and F. Widmer, *ibid.*, 1921, **4**, 174; *A.*, i, 310; M. Samec and J. Matula, *Koll. Chem. Beihefte*, 1919, **11**, 37; *A.*, i, 397; K. Freudenberg, *Ber.*, 1921, **54**, [*B*], 767; *A.*, i, 400; A. Cleve von Euler, *Chem. Ztg.*, 1921, **45**, 977; *A.*, i, 769. " Wood," H. Wislicenus, *Kolloid Z.*, 1920, **27**, 209; *A.*, i, 84; F. Lenze, B. Pleus, and J. Müller, *J. pr. Chem.*, 1920, [ii], **101**, 213; *A.*, i, 163.

[98] A. C. Chibnall and S. B. Schryver, *Biochem. J.*, 1921, **15**, 60; *A.*, i, 482.

[99] H. G. Miller, *J. Amer. Chem. Soc.*, 1921, **43**, 906; *A.*, i, 486; see also next reference.

[1] C. T. Dowell and P. Menaul, *J. Biol. Chem.*, 1921, **46**, 437; *A.*, i, 644.

[2] C. O. Johns and H. G. Waterman, *ibid.*, 1920, **44**, 303; *A.*, i, 84.

[3] D. B. Jones and C. O. Johns, *ibid.*, 291; *A.*, i, 66.

[4] C. O. Johns and C. E. F. Gersdorff, *ibid.*, 1920, **45**, 57; *A.*, i, 212.

[5] Kiyohisa Yoshimura, *J. Chem. Soc. Japan*, 1921, **42**, 16; *A.*, i, 296.

[6] See G. Ciamician and C. Ravenna, *Atti R. Accad. Lincei*, 1920, [v], **29**, i, 416; *A.*, i, 85.

[7] H. E. Annett, H. Das Sen, and H. Dayal Singh, *Pusa Memoirs Chem. Series*, 1921, **6**, No. 1; H. E. Annett, *Biochem. J.*, 1920, **14**, 618; *A.*, i, 87.

[8] For further details of the facts, see A. L. Whiting and W. R. Schoonover, *Soil Sci.*, 1920, **10**, 411.

[9] W. H. Stroud, *ibid.*, 1921, **11**, 123; *A.*, i, 387.

[10] E. B. Fred, *ibid.*, 469, 479.

The function of hydrocyanic acid has been discussed, but no definite conclusion reached.[11]

Colouring Materials in Plants.

The only colouring material of agricultural interest is indigo, which is still grown to an important extent in India. There is some controversy as to the conditions under which the greatest production of indican is obtained; A. and G. L. C. Howard [12] maintain that the yield is improved by organic manures, but not particularly by superphosphate; whilst W. A. Davis insists that phosphates are of prime importance.

The admirable discussion on colouring materials in plants given by Prof. R. Robinson before the British Association at Edinburgh is of very great interest to agricultural chemists.

Calcifuges and Calcicolous Plants.

Plants which fail to grow on calcareous soils are called calcifuges, whilst those which occur there more frequently than on other soils are described as calcicolous. The cause of the difference is obscure (see p. 197), but a promising mode of study has been opened up by M. C. Rayner,[13] which offers possibilities considerably in advance of anything hitherto available. A technique has been devised for growing a typical calcifuge *Calluna* and its associated fungus separately in culture solutions. It is shown that *Calluna* will grow normally in an aqueous extract of a non-calcareous soil, whilst it fails to make such good growth in the extract of a calcareous soil. Clearly, therefore, the soil factor concerned is not exclusively physical, since it is transmitted to the extract; it does not appear to be concerned entirely with the reaction, since the favourable extract was neutral and the unfavourable one only slightly alkaline. It should not prove impossible to trace the cause of the unsuitability of the extract of calcareous soil.

Fertilisers.

As in past years, this branch is dealt with fully in the Report to the Society of Chemical Industry, and only brief reference will be made here to features of special interest.

The problem of increasing the supply of organic matter in the soil

[11] L. Rosenthaler, *Schweiz. Apoth.-Zeit.*, 1920, **48**, 137; 1921, **49**, 10, 22; *A.*, i, 484; P. Menaul, *J. Biol. Chem.*, 1921, **46**, 297; *A.*, i, 484.

[12] *Pusa Mem. Bot. Series*, 1921, **11**, No. 1.

[13] M. C. Rayner, *J. Ecology*, 1921, **19**, 60.

has been attacked by ascertaining the conditions under which straw decomposes to form humus, and then carrying out the decomposition on the farm. The necessary conditions are, air and water supply, a nitrogen nutrient for the organisms effecting the decomposition, and sufficient calcium carbonate to ensure neutrality. It is claimed that an effective fertiliser can be produced from straw in this way, and that the process can be worked on farms where insufficient farmyard manure is obtained during the ordinary operations.[14]

Much interest has been aroused in technical circles by the announcement in Germany that artificial enrichment of the atmosphere in carbon dioxide was being practised successfully as a means of increasing plant growth both in glasshouses and in the open. A patent has been taken out for absorbing this gas from flue and furnace gases, then evolving it and delivering it in pipes near to the roots of plants. So much interest has been aroused that the method will probably be tested in this country.[15]

E. J. RUSSELL.

[14] H. B. Hutchinson and E. H. Richards, *J. Min. Agric.*, 1921, **28**, 398.

[15] F. Bornemann, " Kohlensaure und Pflanzenwachstum," Parey, Berlin, 1920; F. Riedel, *Stahl u. Eisen*, 1919, **40**, 1497; *Möllers Deut. Gartner Ztg.*, July 20 and 30, 1921, where some illustrations are given; *Chem. Ztg.*, 1920, 585, 808.

CRYSTALLOGRAPHY AND MINERALOGY.

THERE is a very considerable amount of fruitful research in these domains of science to record as the product of the year 1921. After a short respite, during which it appeared as if grave difficulties were accumulating in the path of further progress in elucidating the structure of crystals by means of X-rays, a remarkable step forward has been taken, both as regards new methods and new ground, that of organic chemistry. It will be convenient to commence with the latter most interesting departure first, although its publication has only occurred as this Report is being sent in. By the great kindness of Sir William Bragg, however, the writer was supplied with the proof-sheets, and also had early access to the models.

X-Ray Analysis of Organic Substances.

An attempt had already been made by R. O. Herzog and W. Jancke[1] to obtain information concerning the structure of some organic compounds of the fatty series by means of the X-ray powder method of Debye and Scherrer, but the difficulties met with appear to have been very great, the interpretation of results proving well-nigh insuperable. Cellulose appears to have afforded the least ambiguous results, the elementary monoclinic cell of the space-lattice of the crystals of this substance having been found to contain four dextrose residues, which are of two types, two being of each type.

But on November 11th (1921) Sir William H. Bragg,[2] in his Presidential Address to the Physical Society, which the writer was privileged to hear, announced the first result of a much more successful attack on organic substances, by means of his own methods of X-ray analysis. He was led to begin with a few of the better crystallising aromatic compounds, especially naphthalene and its derivatives, and for a reason which in itself is highly interesting. It will be remembered that the elucidation of the structure of the diamond was one of Sir William's early successes, and sub-

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[1] R. O. Herzog and W. Jancke, *Z. angew. Chem.* 1921, **34**, 385; *A.*, ii, 531.
[2] Sir W. H. Bragg, "The Structure of Organic Crystals," *Proc. Phys. Soc.*, 1921, **34**, 33.

sequently Debye and Scherrer, and independently A. W. Hull, discovered the structure of graphite, by means of the powder method, and found it to be a trigonal one which is illustrated by the model of which a drawing is shown in continuous line in Fig. 1. Now the remarkable thing is, that if the top layer of the model be moved to the closer and rotated position indicated by the dotted lines, the structure of the diamond is obtained. It will be recalled that in diamond the carbon atoms are arranged on a face-centred cube lattice, with also an atom in the centre of every alternate one of the eight cubelets into which the main cube is divided. It thus consists of a series of puckered layers parallel to any given plane of the tetrahedron, and each carbon atom is attached to four others. The diamond cleaves along these layers.

FIG. 1.
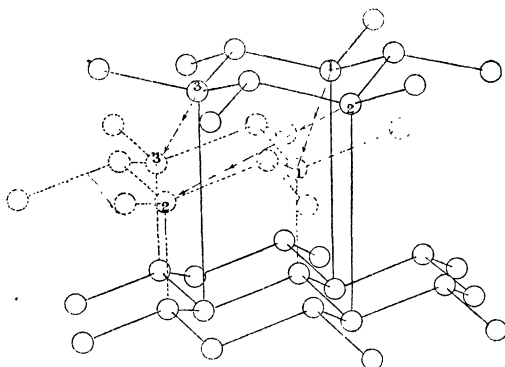
Conversion of Graphite to Diamond Structure.

The structure of graphite shown in Fig. 1 is conversely afforded by taking two such layers of the diamond model and moving one of them away from the other, to the position corresponding to that in Fig. 1. The exact configuration shown, in which the lines are puckered, is that given by Hull, whereas Debye and Scherrer place them in the same plane. Whether puckered or plane, however, these layers are clearly composed of six-carbon-atom rings. Now the very strong bonds between the atoms of these rings in the layers of a diamond not only persist in the graphite structure, but are drawn somewhat tighter, while the distance separating the layers in the latter is much greater than in the more symmetrical diamond; the cohesion is thereby so much lessened between the layers that graphite is one of the softest of substances, not only splitting readily in layers, but actually being useful as a lubricant. On the other hand, diamond is the hardest substance known. The

shortest distance between each pair of carbon atoms lying in the same layer in the diamond is 1·54 Å.U., while in graphite it is shortened to 1·50; but the distance between two successive layers is increased by 1·35 Å.U., so that a carbon atom in graphite is now equally distant from its three nearest neighbours of the next layer, namely, by the relatively large amount of 3·25 Å.U., according to Hull.

These interesting facts regarding elementary carbon have caused Sir William Bragg to believe that the hexagonal rings, which persist even in graphite, do so also throughout the aromatic compounds. He therefore assumes the benzene ring to be such a simple hexagonal ring, more or less puckered, of carbon atoms, whilst naphthalene is composed of double rings, and anthracene of triple rings. Using Hull's spacings, the arrangement in naphthalene he

FIG. 2.
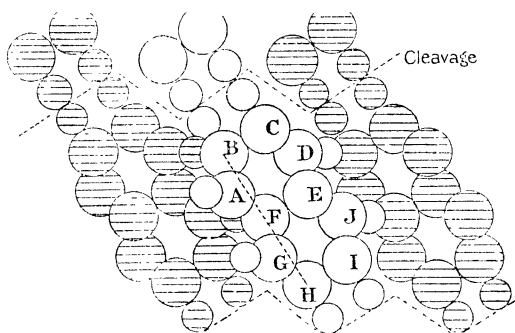
The Structure of Naphthalene.

considers to be that shown in Fig. 2, which includes three naphthalene molecules and parts of others. The ten carbon atoms, from A to J, form the double ring corresponding to one molecule of naphthalene, while the six atoms $A\,B\,C\,D\,E\,F$ form a benzene ring. The centres of the atoms A and G are 0·71 Å.U. above the plane, and the centres of D and J the same distance below the plane of the diagram, those of the rest of the atoms lying in the plane itself.

Benzene is not an easy substance on which to commence the attack, as it is only solid below 6°, its melting point. It is interesting to recall, however, that Debye and Scherrer believed that they had obtained evidence that the molecule of benzene has the form of a hexagonal tablet, the edge of the regular hexagon having the length 6·02 Å.U., and the thickness of the tablet being 1·19 Å.U. Naphthalene, $C_{10}H_8$, crystallises in the holohedral, prismatic, class 5

of the monoclinic system, possessing both the digonal axis of symmetry and the plane of symmetry perpendicular to it, the ratio of the axes being $a : b : c = 1\cdot3777 : 1 : 1\cdot4364$, and the axial angle β being $122° 49'$. The very perfect cleavage is parallel to the basal plane (001), and the other principal faces developed are (110), (20$\bar{1}$), and (11$\bar{1}$). The density is low, $1\cdot152$.

The first results afforded by the X-ray spectrometer indicate that the space-lattice of both naphthalene and anthracene is No. 13, the unit cell of which consists of a parallelepipedon with two pairs of rectangular faces, inclined at the axial angle β, and one pair of rhomboidal ones, as shown by the two cells in Fig. 3, the dimensions for naphthalene being $a = 8\cdot34$, $b = 6\cdot05$, $c = 8\cdot69$ Å.U. It was next found that two molecules are contained in each cell, the knowledge being derived in the usual Bragg manner from the density,

FIG. 3.

NAPHTHALENE   ANTHRACENE
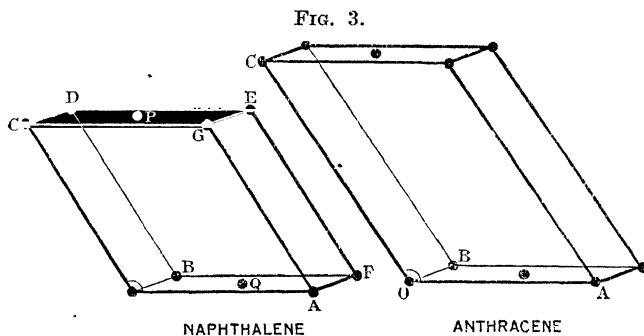
Unit Cells of Naphthalene and Anthracene.

the actual weight of the molecule, the axial ratio, and the X-ray measurements; for it was found that the (100) and (010) spacings are only half what they should be if each corner of the cell represented a single molecule; for only one-eighth of a corner molecule is assignable to this particular cell, each corner being the point of contact of eight adjacent molecules, so that the whole eight parts correspond together to one whole molecule within the cell. But the spacing of (001) agrees, so there must also be a molecule at each of the points P and Q in Fig. 3, each contributing half a molecule to the cell.

On proceeding next to anthracene, $C_{14}H_{10}$, the crystals cannot be used similarly for the single crystal method, as they are only small flakes; but by pressing a number of them against a flat disc, so that all their (001) planes were parallel thereto, a determination of the (001) spacing was found possible, and the linear dimensions of the unit cell were determinable. The crystallographic axial ratio of anthracene is $a : b : c = 1\cdot4220 : 1 : 1\cdot8781$, the axial angle

is 124° 24', and the density 1·15. There were found to be two molecules to each unit cell, as in the case of naphthalene, and the dimensions afforded by the X-ray measurements were $a = 8·7$, $b = 6·1$, and $c = 11·6$. These values, as regards a and b and the axial angle, were nearly the same as for naphthalene, but the c-length was 2·9 Å.U. greater.

Now this result is of the greatest importance, for if we accept that the double-ring naphthalene molecule at each corner is replaced by the three-ring molecule of anthracene the increase in size should be about 2·5 Å.U. per molecule. Sir William Bragg concludes, therefore, that the double- or triple-ring molecules lie along the vertical c-axis, and that the anthracene cell is longer than that

FIG. 4.
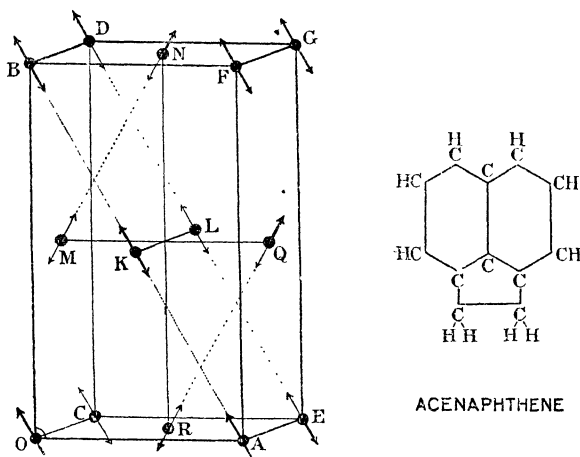
Unit Cell and Constitutional Formula of Acenaphthene.

of naphthalene by the observed amount for this reason. The lengths of the molecules of the two hydrocarbons, without allowing for the hydrogen atoms, are 6·41 and 8·86 Å.U. respectively, so that there is a vacant space between the ends of the molecules for the accommodation of the two β-hydrogen atoms. As regards the position of the plane of the double- or triple-ring molecule, which must contain the c-axis, all the indications point to the probability that it approximates to the (010) symmetry plane ac, that the β-hydrogens of one molecule lie up against the corresponding ones of the next molecule, and that the (001) plane passes through them all. This (001) plane is then naturally the plane of cleavage, as is actually observed, the atoms being condensed and strongly attached in the rings in the plane, and the cohesion a minimum in the perpendicular direction. The α-hydrogen atoms, those on the sides

of the double- or triple-ring molecule, lie up against the carbon atoms of the neighbouring molecules, and there is about 1 Å.U. of space for them, an adequate amount.

The forces between the molecules are weaker than the valency forces, and of these weaker forces those between the β-hydrogen atoms are weaker than those between the α-hydrogen and carbon atoms. But these two weaker sets of forces are those which bind the molecule into the crystal. The structure thus arrived at is a very open one, as will be clear from Fig. 2, in which the smaller circles represent the hydrogen atoms.

Three derivatives of naphthalene have also been studied, acenaphthene and the α- and β-naphthols. A most interesting result has been afforded by acenaphthene, the structure and constitution

FIG. 5.

Unit Cell and Constitutional Formula of a-Naphthol.
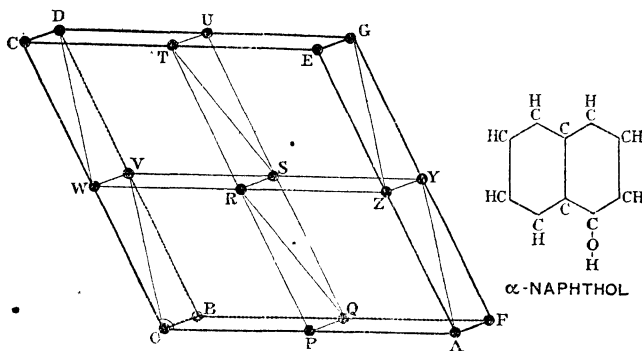
of which are shown in Fig. 4. While the molecule has been made lop-sided by the substitution of $2CH_2$ for the two hydrogen atoms on one side, the crystal itself is of higher symmetry than that of naphthalene, being holohedral orthorhombic (class 8), with the axial ratio $a : b : c = 0.5903 : 1 : 0.5161$. The X-ray analysis has shown that there are in this case not two but four molecules in the unit cell of the space-lattice, the sides of which have the absolute lengths $a = 8.32$, $b = 14.15$, and $c = 7.26$ Å.U. In fact, the enhancement of the symmetry, compared with that of naphthalene, has been produced by two of the four unsymmetrical molecules being arranged mirror-image-wise with respect to the others, across one of the principal planes. There is a molecule at each corner of the cell, and also one in the middle of each face. Those at the corners and also those at K and L lie parallel to AB, while those at M, N, Q, and R, which between them contribute to the cell the other

two molecules which belong to it, slope the other way, parallel to *MN*, while lying in the same plane.

Considering now α-naphthol, this substance forms monoclinic crystals of the holohedral prismatic class 5 like naphthalene, with an axial ratio of $a : b : c = 2.7483 : 1 : 2.7715$, and an axial angle 117° 10′. Its density is 1.224. There are found to be four molecules in the unit cell, which has the absolute dimensions $a = 13.1$, $b = 4.9$, and $c = 13.4$ Å.U., and which is represented in Fig. 5. These lop-sided molecules are placed as shown in the figure, and they lie with their double-ring lengths " criss-cross," as represented by the diagonal lines, but they now lie edge-ways on top of one another instead of flat-ways, the *a*-axis and not the *c*-axis running

FIG. 6.
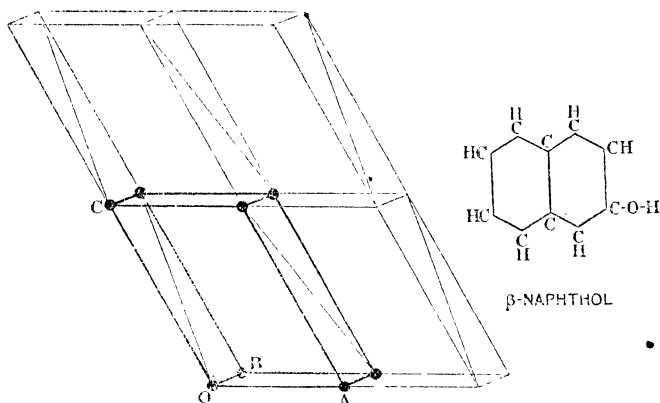
Unit Cell and Constitutional Formula of β-Naphthol.

along the line of crossings. The cleavage plane, however, again passes through the β-junction. The hydrogen atoms fit very naturally into their places, and link the tops of the molecules together in one (001) layer and the bottoms in the next layer. The hydroxyl groups are thus brought rather close to each other, as if the attraction were between the oxygen atoms.

It has only been possible to investigate the powder of β-naphthol, but this has been adequate to fix the absolute dimensions of the monoclinic space-lattice unit cell. Fig. 6 shows this lattice and also the constitutional formula. The axial ratio is $a : b : c = 1.3662 : 1 : 2.0300$, and the axial angle 119° 48′. The cell dimensions are $a = 5.85$, $b = 4.28$, and $c = 8.7$ Å.U. It is found that only one molecule goes to a cell, but it is the small (quarter) cell indicated by strong lines in the figure. The removal of the hydroxyl group from the side to the end of the molecule has caused

the cell to shrink in its lateral dimensions and to grow along the vertical axis, thus affording a striking confirmation of the assumption that the molecules lie lengthwise along the vertical c-axis. The cleavage plane still cuts along the β-hydrogen junctions. This quarter cell, however, does not account for the full symmetry, for the dissymmetry of the single molecules would lower the crystallographic symmetry; the four cells containing together four molecules, as in α-naphthol, are requisite to account for the holohedral symmetry of the crystal, and so the large cell of the figure, containing four molecules, is to be considered as the unit cell of the space-lattice, the " grosser unit " of the crystal structure as the writer terms it, exhibiting the true symmetry of the crystals of the substance in question. The hydroxyl groups are drawn together, so that pairs of molecules point opposite ways. The structure is thus essentially similar to that of α-naphthol.

A more limited study was found possible of α-naphthylamine, a unit cell of almost exactly the same rectangular shape and dimensions as acenaphthene being revealed, which contains four molecules and has the dimensions $a = 8·62$, $b = 14·08$, $c = 7·04$ Å.U., but a and c are interchanged in the two substances. The length of the molecule works out to be : for α-naphthylamine 8·25, for acenaphthene 8·23, and for α-naphthol 8·31. The lop-sided molecules in all three cases are laid criss-cross on one another, whereas in naphthalene itself they are arranged parallelwise, and the somewhat different length, 8·7, of the naphthalene molecule is a consequence.

Until benzene itself has been investigated, which will involve special low-temperature arrangements, the well-crystallising benzene derivatives cannot be fully worked out, but as regards benzoic acid it has been established that the (001) spacing is quite exceptionally wide, 10·9 Å.U., and that sheets of molecules lie in these (001) planes at this wide distance apart, the dimensions of the cell, which contains four molecules, being $a = 5·44$, $b = 5·18$, $c = 21·8$ A.U., and the axial angle 97° 5'. Moreover, the sheets differ alternately, and the bridging appears to occur by the COOH extended groups, a CO extension from one ring probably joining on to an OH extension from another ring. These bridges, however, are very flimsy, and the crystals consequently flake at the least touch. The powder method had to be used because of this property.

The Bearing of these New Results on Molecular Structure.

These interesting results with aromatic organic substances are considered by Sir William Bragg to agree extremely well with the work of Langmuir. The forces that bind atoms together are clearly shown to be of more than one kind. The very strong valency

bonds, whether due to electron sharing or other causes, are exemplified by all the linkings between the carbon atoms of the diamond, and also by those in the planes of the flakes of graphite. Quite different, however, are the much weaker bonds between an atom in one graphite sheet and its three nearest neighbours in the next sheet. It is this weaker second kind of bond which unites the molecules of the organic compound so as to form the crystal. The cleavage is the indication of their weakest direction. These weaker bonds are definitely associated with special points on the molecule.

" When a crystal forms in a liquid, or by sublimation, the molecule that attaches itself correctly, and with proper orientation to others already in position, is the one that stays there and resists the tendencies of other drifting and thermally agitated molecules to remove it. It is fixed by the attachment of certain points on its own structure to certain points on the structure of the other molecules. The beautiful exactness of crystal structure is evidence of the precision with which this adjustment is made; and at the same time of the definite molecular form without which precision would be impossible."

In the case of naphthalene the molecules arrange themselves side by side, the α-hydrogens of each molecule seeking to attach themselves to the carbon atoms of its neighbours, no valency bonds being concerned. This side-to-side combination is preferred to the end-to-end attachment, so that a crystal grows quickly out into thin sheets. Moreover, the particular geometry may permit a molecule to attach its active points to those of other molecules in more than one way, producing twinning rather than a continuation of the previous regularity.

The surface films studied by Langmuir, Adam, and others were not aromatic compounds, but they exhibited similarly strong side-to-side attachments of their molecules as compared with end-on attachments. A film of oleic acid, for instance, is formed on water when the hydroxyl ends of some of the molecules root themselves in and are held quietly by the water, while other molecules link on side by side and the film thus spreads over the water. The arrangement parallelwise of the long-chain molecules, the swarm of Bose, of the substances forming the " liquid crystals " of Lehmann is probably similar, ammonium oleate, $C_{18}H_{33}(NH_4)O_2$, being one of the best known cases, the length of the molecules themselves in these long-chain compounds facilitating the process.

Sir William Bragg finally concludes that " the arrangement of molecules in crystals . . . cannot be fully explained as due to forces which are merely functions of the distances between their centres. Confining ourselves to cases where there is no obvious separation

of electron charges, as there is none in the crystals described above, it is clear that we must think of molecules as bodies of very definite form. These attachments to one another are made at definite points, and the forces there exerted may have very short ranges. The molecules are locked into crystal structure when attachments are made at sufficient points, and the whole has the stability of an engineering structure."

This very clear result of Sir William Bragg's work on the aromatic carbon compounds will materially assist in correcting the very premature statements that have been made by some authors, even by Prof. von Groth, soon after the first results of X-ray analyses of very simple binary compounds and elementary substances were published, that chemical molecules do not exist in the crystalline condition.

The present writer [3] has felt impelled to protest strongly against this very improbable conclusion, and has pointed out that " there can be no question but that the growth of a crystal is to be attributed to the special properties of the surface of the solid crystal already laid down, whereby further accretions of growth occur," and that " the whole process of the passage from liquid to crystal is so continuous, and the natural succession of phases—gas, liquid, liquid crystal, and true solid crystal—follow so unbrokenly, that to deny the continued existence of the molecule at any stage is illogical.

" The fact that the persistence of the molecule is not absolutely essential to the geometrical explanation of crystal structure is not a valid argument for denying that persistence. . . . The close approximation of the molecules in the act of crystallisation may yet occur without destruction of the interatomic forces which retain the molecules as such. There may be a certain amount of pooling of the chemical affinities when the atoms are brought into such close neighbourhood that those belonging to different molecules are little if any further removed from each other than those of any one and the same molecule; indeed it is likely that these forces exerted at close quarters by the atoms of one molecule on those of other approaching molecules together constitute the directive force of crystallisation, which determines the type of crystal structure produced. In any case, at the first opportunity, such as that afforded by solution or fusion, for instance, the same molecules or others indistinguishable from them are again restored as freely moving separate entities. Also only concentrated, indeed supersaturated, and not dilute, solutions are concerned in crystallisation, so that electrolytic dissociation and ionisation are excluded."

[3] A. E. H. Tutton, " Crystallography and Practical Crystal Measurement," 2nd edition, now on point of publication, Macmillan and Co.

different orders at a given crystal facial plane, and (c) an attempt to locate the exterior electrons of the atom.

Application of the Powder Method to the X-ray Spectrometer.

With respect to (a) it should be made clear that there are two distinct methods of using the X-rays for crystal investigation. In one, the original method, a single crystal is employed, and the experience now acquired shows that the relatively large size of crystal employed during the early work is by no means essential; the crystal need not weigh more than a few milligrams, and it is actually more convenient that it should be small, for the pencil of reflected rays is then conveniently limited without the need for slits other than to act as stops. This method is still the best and most valuable and instructive.

The other method, in which crystal powder is employed, is of great value when good, small, isolated crystals are not available. All the spectra from the different planes of atoms effective are thrown together on the same photographic film or plate, and require to be disentangled, a process which has been much simplified by Sir William Bragg. Instead of using the cylindrical camera of Debye and Scherrer, at the axis of which lies the cylindrical tube or capillary containing the crystal powder, he pastes the powder on a flat surface and places the latter, instead of the crystal, on the X-ray spectrometer. A Muller X-ray bulb is most suitable for use with this method, actuated by a half-kilowatt transformer. The spectrometer slit is brought close up to the radiator, becoming thereby the source of a very powerful beam of X-rays sufficiently divergent to cover a relatively large surface of the plate on which the powder is spread. The anticathode is preferably of copper, as the long wave-lengths of the copper K-series of X-rays give suitable angles of deflection even for the wide spacings that are found in organic crystals. The method is especially suitable for organic crystalline substances, many of which can only be obtained in very small, flaky, acicular, skeletal, or otherwise imperfect forms, useless for the single crystal method.

The Interpretation of Intensity of X-ray Reflection.

The very difficult question (b) of the correct determination and interpretation of the intensity of X-ray reflection in the different orders, from a plane of atoms in a crystal, has been specially investigated by Prof. W. L. Bragg,[5] in collaboration with R. W. James

[5] W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.*, 1921, [vi], **41**, 309; **42**, 1; *A.*, ii, 477.

and C. H. Bosanquet. Very purely homogeneous X-rays were first obtained, by preliminary reflection, from a crystal of rock-salt, of the rays from an already fairly pure source, such as the 0·584 Å.U. radiation from a palladium anticathode. A diagram of the arrangement is given in Fig. 7. Such preliminary reflection (from the crystal C_1) at the correct glancing angle eliminates all other undesirable general radiations, and the intensity of the very pure ray thus obtained can be measured with considerable accuracy. When this pure ray of known intensity is allowed to fall on the crystal under investigation C_2 at the proper glancing angle for that crystal the reflected beam can be investigated as to its exact intensity with great confidence. The ray is directed exactly to the first crystal face C_1 by the leaden wedge W, round which the reflection occurs; and the second crystal C_2 is rotated with uniform velocity, and the total amount of radiation reflected is measured in the usual way. From a considerable amount of experimental work on these lines, using rock-salt and a number of other suitable well-crystallised substances, a formula of a comprehensive character has eventually been derived, as the expression of the reflecting power of a crystal plane. It includes factors due to the work of Debye and Scherrer, Darwin and Compton, and of Sir W. H. Bragg, derived both from theoretical considerations and from exact measurements. It is as follows :
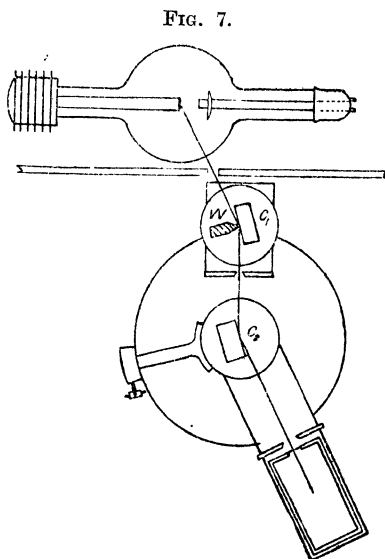
FIG. 7.

Arrangement for Determination of Intensity of Reflected X-rays.

$$R = \frac{N^2\lambda^3}{2\mu \sin 2\theta} \cdot F^2 \frac{e^4}{m^2c^4} \cdot \frac{1 + \cos^2 2\theta}{2} \cdot e^{-B\sin^2\theta},$$

in which R is the reflecting power of the face (plane of atoms), N is the number of atoms per unit volume, λ the wave-length of the X-rays, θ the glancing angle of reflection, μ the linear absorption coefficient of the X-rays in the crystal substance, e the charge and m the mass of an electron, c the velocity of light, B a constant determined by Sir William Bragg to be 4·12, and F a factor depending

on the angle of scattering and the number and arrangement of the electrons of the diffracting atom. This interesting factor F has its maximum at a very small angle of scattering and falls off as the glancing angle increases, owing to interference between the wave-trains diffracted by separate electrons. By comparing the theoretical formula with the measurements obtained by experiment it is possible, since all the other constants are known, to determine this factor over a range of angles, and thus obtain valuable information concerning the arrangements of the electrons in and around the atom, and in particular concerning the positions of those composing the outer shell.

The results as published in the two papers quoted agree with the Lewis-Langmuir version of the atomic structure theory. The experimental work with sodium chloride, for instance, afforded measures of the intensity of reflection of (amplitude of the X-rays diffracted by) the chlorine and sodium atoms separately over a range of angles from $10°$ to $60°$, and also indicated the correct number of electrons in the atoms of each element, and that they are distributed in shells. In a contribution to the discussion on Dr. Langmuir's address to the British Association in September (1921), however, Prof. Bragg stated that the distribution indicated was one in which the inner shells of electrons were somewhat closer to the nucleus than was expected.

Attempt to Locate Exterior Electrons of Atoms.

The third new departure (c) is of a still more fascinating character, the direct application of the X-ray spectrometric method to the location of the outer electrons of the atom, thus even more directly experimentally than as described under (b) going beyond the crystal structure to that of the atoms composing it. The work is described in two papers by Sir William H. Bragg [6] and Mr. H. Pealing. [7] Sir William Bragg, and also Debye, had for some time been considerably exercised as to the existence or otherwise of a weak second order spectrum from the tetrahedral planes of the diamond, but at last Sir William has definitely observed it. The fact is of great importance as it determines that alternate planes of carbon atoms are not alike, and that the carbon atom has in itself a tetrahedral arrangement of electrons, and not a sphere with similar properties in every direction from the centre, but is tetrahedrally differently disposed, as if there were connecting electrons thus arranged between the atoms. This further implies something tetrahedral in the atom itself, for the electrons to fit on to. ,

[6] Sir Wm. H. Bragg, *Proc. Phys. Soc.*, 1921, **33**, 304.

[7] H. Pealing, *ibid.*, 297.

Mr. Pealing studied fluorspar in a similar manner and obtained analogous results. It will be remembered that the calcium atoms occupy the points of a face-centred cube lattice, and the fluorine atoms the centres of the eight cubelets into which the calcium cube may be divided. As the atomic weight of calcium (40) almost exactly balances the weight of two fluorine atoms ($2 \times 19 = 38$), the first-order spectrum from the cube planes is nearly extinguished. But the third-order, instead of being still more completely neutralised, is much more intense, indicating the presence of some weak diffracting centre about one-third or one-fourth of the way between calcium and fluorine planes, and these appear to be singularities at the points of junction between the calcium and fluorine atoms, probably connecting electrons.

Hence, these experiments clearly point to the existence of stationary electrons, or at least of electrons having average positions which are not central but have other definite stations. Further, they show that the atoms in the crystal are not packed into the smallest possible volume, but form a structure in which relatively large empty spaces are left. In the case of the diamond each atom is surrounded by only four neighbours, whereas there would be twelve in the close-packed arrangement of similar atoms; indeed, the structure is so hollow that an additional equal number of atoms could be accommodated in a given space, the arrangement then becoming that of the centred cube, in which each atom has eight neighbours.

These results are also in agreement with the Lewis-Langmuir version of the atomic structure theory. For the carbon atom of the diamond is shown to have four special directions or positions of attachment of one atom to the next, corresponding with its quadrivalency. And as regards fluorspar, the results agree with the supposition of Langmuir, on the same principle as already explained for sylvine, that a calcium atom of atomic number 20 has two extra (valency) electrons above the 18 needful to form the stable argon shell of 18 electrons, and will thus combine with two fluorine atoms of atomic number 9, having one electron each less than required to form the stable neon arrangement of 10 electrons, to produce a compound having the stable shells corresponding to argon and neon around their nuclei.

All this recent crystallographic X-ray work is thus so intimately bound up with the Lewis-Langmuir generalisation that it is essential that a brief account should here be given of the relevant portion of Dr. Langmuir's address to the joint Chemical and Physical Sections of the British Association at the late (September 1921) Edinburgh meeting.

The Lewis-Langmuir Theory as expounded by Dr. Langmuir.

The writer, who was present on the occasion, gathered that there are three main assumptions. The first is that the electrons in atoms surround the nucleus in successive layers, shells, or sheaths containing 2, 8, 8, 18, 18, and 32 electrons respectively, their ratio being as $1^2 : 2^2 : 2^2 : 3^2 : 3^2 : 4^2$. The second is that atoms may be coupled together by one or more " duplets," or pairs of electrons, held in common by the completed sheaths of the atoms. The third is that the residual charge on each atom and on each group of atoms tends to a minimum.

Experimental evidence was given by Dr. Langmuir, such as that derived from vapour-density determinations of the liquid carbonyls, that the number of electrons in the various shells is as given above and not that assumed in the Bohr-Sommerfeld version (2, 8, 18, 32, 18, 8). It was also pointed out that the sharing of a duplet (pair) of electrons by two atoms corresponded to what has become known as co-valency, and that this kind of bond is that met with, for instance, in the organic compounds; and that the bonds chiefly met with in inorganic compounds are those of electro-valency, supposed to be due to an electron or electrons passing from the sheath of one atom to that of another. The first type indeed (which shares electrons) usually occurs between two electro-negative elements, and the second type between an electro-positive and an electro-negative element. A chemical combination is represented in general form by Dr. Langmuir by the equation

$$\Sigma v_e + \Sigma v_c = 0 ,$$

where v_e is electro-valence and v_c is co-valence : also $v_e = e - s$, where e is the kernel (nuclear) charge and s is the number of electrons in the complete sheath, 8, 18, or 32.

Dr. E. K. Rideal pointed out that the very opposite assumptions of a static character in the Langmuir atom, and of a dynamic character in the Bohr atom, may be reconciled by regarding the atoms as static except during the actual emission or absorption of energy, oscillation of the electrons under these conditions being more probable than rotation. Indeed there is a general feeling prevalent that eventually the Lewis-Langmuir and Bohr-Sommerfeld versions of the atomic structure theory will be brought together, and give us between them a fuller expression of the truth. The history of science is rich in such cases. It would even appear as if an important step in this direction has been taken by Sir J. J. Thomson in his latest paper (*Phil. Mag.*, 1921, [iv], **41**, 510), in which he shows that his results agree with the law of atomic diameters of

W. L. Bragg, and with Langmuir's version so far as the character and number of electrons in the outer shells are concerned. But no sharing of electrons is assumed, molecules being supposed to be formed by the outer electrons simply acting as couplings, each valency bond requiring two electrons, one belonging to each atom, and a double bond being formed by four electrons arranged at the corners of a square at right angles to the line joining the atomic centres. These views appear to offer a good explanation of the benzene ring, and are favourably received by many organic chemists.

Prof. A. O. Rankine adduced some interesting facts in support of Dr. Langmuir's assumptions, from his experimental determinations of the viscosity of gases. In the first place his results lead to a diameter of the chlorine molecule which is practically identical, as it should be according to the Langmuir version, with the added diameters of two argon atoms, the outer shells of which are in contact; also to similar results with respect to bromine and krypton, and with regard to iodine and xenon. In the second place, a remarkable additional significance was pointed out, of the fact discovered by the present writer during the course of his crystallographic investigation of isomorphous series (sulphates, selenates, and double salts), namely, that analogous ammonium and rubidium salts are practically isostructural, their molecular volumes and the dimensions of their space-lattice unit cells being almost exactly the same. Rankine assumes, therefore, from this fact that rubidium and ammonium possess equal molecular volumes, and that if the Langmuir version be correct krypton should bear the same relation to rubidium as methane, CH_4, bears to ammonium, NH_4, and an atom of krypton should have the same volume as a molecule of methane. Actual determinations by Rankine of the volumes of krypton and methane by the viscosity method agree with this precisely.

It is of more than merely passing interest that this fact of the isostructure of the rubidium and ammonium compounds should prove of such use. The fact has been verified over and over again during the course of the writer's work, no less than eighteen cases having been studied; and it is confirmed once more in the final instalment, on the manganese and cadmium groups, of the research on the double selenates, which the writer has just completed, so that no exceptions for the oxy-salts (sulphates, selenates, doublesulphates, -selenates and -chromates) are now possible. It was fully substantiated by the absolute measurements made with the writer's crystals in Sir William Bragg's laboratory by Prof. A. Ogg and Mr. F. L. Hopwood [8] of the space-lattice cells of ammonium and

[8] A. Ogg and F. L. Hopwood, *Phil. Mag.*, 1916, [vi]. **32**, 518; *A.*, 1916, ii, 594.

rubidium sulphates. It was this same fact which afforded con-
clusive evidence of the fallacy of the valency volume theory of
Sir William Pope and Mr. W. Barlow; for if that theory were correct
the volume of the ammonium sulphate cell should be twice that of
the unit space-lattice cell of rubidium sulphate. The law of atomic
diameters of Prof. W. L. Bragg, which affords the true sizes of the
atoms, and is so fully confirmed by the work of Rankine, now re-
places the theory of Pope and Barlow, and with this law the writer's
results for isomorphous series are in complete agreement.

Bragg's Law of Atomic Diameters.

This law, which had only just been announced by Prof. W. L.
Bragg [9] when last year's Report was written, and could be only

FIG. 8.

Atomic Numbers of the Elements.
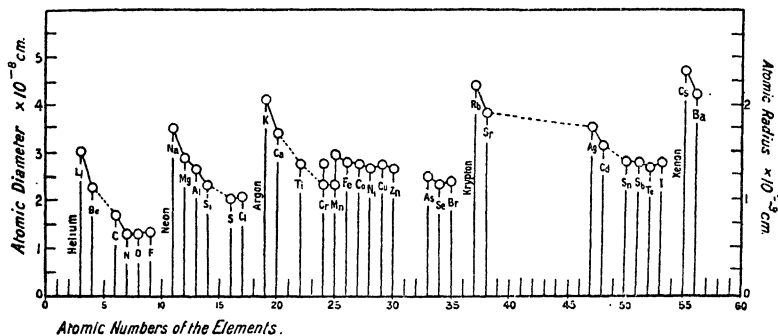
The Curve of Atomic Diameters.

briefly and incompletely referred to, has received further experi-
mental support during 1921. A careful scrutiny of all the absolute
measurements of atomic-plane spacing and atomic distances in
crystal structures, carried out up to the present by means of X-rays,
has confirmed the first assumption that the atoms of each element,
when regarded as spheres, possess the same diameter in all the
cystallised compounds into which they enter, and that these constant
atomic spherical dimensions are related, not as the valencies of the
elements (the Pope and Barlow hypothesis), but in the manner
graphically exhibited by the periodic curve reproduced from Prof.
Bragg's memoir in Fig. 8. When the crystal is that of a chemical
element the distance between the centres is actually the diameter
of the sphere itself, the sum of the radii of the two equal spheres in
contact; and when it is that of a chemical compound the distance

[9] W. L. Bragg, *Phil. Mag.*, 1920, [vi], **40**, 169; *A.*, 1920, ii, 537.

separating the centres of two adjacent atoms of different elements is the sum of the two radii of the spheres, now different.

In all cases, in fact, the distance between the centres of contiguous atoms, whether of the same or different elements, is equal in absolute measure to the sum of the two atomic radii. These distances, moreover, correspond with the observed closest positions of the two elementary atoms, nearer than which they never approach, the limiting surface of each being apparently that of the outer shell of electrons, or at any rate that of a sphere of impenetrability, the atomic domain. A table of the actual values is next given, as derived from direct X-ray measurement with crystals, and it also includes the diameters of the atomic spheres of neon, argon, krypton, and xenon, derived from indirect determinations of the outer shells of electrons.

ATOMIC DIAMETERS, IN ÅNGSTRÖM UNITS.

$$\text{Å.} = 10^{-8} \text{ cm.}$$

Atomic number.	Element.	Atomic diameter.	Atomic number.	Element.	Atomic diameter.
3	Lithium	3·00	26	Iron	2·80
4	Glucinum	2·30	27	Cobalt	2·75
6	Carbon	1·54	28	Nickel	2·70
7	Nitrogen	1·30	29	Copper...........	2·75
8	Oxygen	1·30	30	Zinc	2·65
9	Fluorine	1·35	33	Arsenic	2·52
10	Neon	1·30	34	Selenium	2·35
11	Sodium	3·55	35	Bromine	2·38
12	Magnesium ...	2·85	36	Krypton	2·35
13	Aluminium ...	2·70	37	Rubidium	4·50
14	Silicon	2·35	38	Strontium	3·90
16	Sulphur	2·05	47	Silver	3·55
17	Chlorine	2·10	48	Cadmium	3·20
18	Argon	2·05	50	Tin	2·80
19	Potassium	4·15	51	Antimony	2·80
20	Calcium	3·40	52	Tellurium	2·65
22	Titanium	2·80	53	Iodine	2·80
24	Chromium	2·80	54	Xenon	2·70
	″ { (electro- \ (negative) } 2·35		55	Cæsium	4·75
			56	Barium	4·20
25	Manganese	2·95	81	Thallium	4·50
	″ { (electro- \ (negative) } 2·35		82	Lead	3·80
			83	Bismuth	2·96

In making these comparisons from all the published material, and with the aid of new determinations of atomic diameters by Prof. Bragg himself, of which the results are expressed in the table, it has been clearly recognised that there are two very distinct types of structure in crystals, namely, (1) those in which the relative positions of all the atoms are fixed by the symmetry, and (2) those in which, while some atomic positions are fixed, those of other atoms are not but, within certain limits (usually along a line) which are dependent on the symmetry, are permitted some latitude of arrange-

ment, the exact positions being determinable by the X-ray measurements. The chlorides of sodium and potassium, zinc blende, and the diamond, are obviously of the first type; and iron pyrites of the second. For while the iron atoms in pyrites are fixed at the corners and face-centres of the cube, the sulphur atoms are situated on alternate diagonals, at a definite position on each of these diagonals which is not, however, fixed by the symmetry but has been found by X-ray measurement to be at the distance of 1·025 Å.U. from an unoccupied corner of the cubelet, eight of which cubelets form the main cube which has iron atoms at its corners and face-centres. Indeed, as there is another sulphur atom on the continuation of this same diagonal in each case, at the same distance from and on the other side of the unoccupied corner just referred to, the centres of these two sulphur atoms will be at the distance apart of 2·05 Å.U. Further, as sulphur atoms have never been found to approach closer than this, 2·05 Å.U. is the sum of the two radii and therefore the atomic diameter of sulphur.

The next striking fact brought out by the law of atomic diameters is that the electro-positive alkali metals, lithium, sodium, potassium, rubidium, and cæsium stand out with remarkable prominence at sharp maxima of the curve, which is steep on each side of them; the alkaline earths follow some distance down, whilst the electronegative elements and those dyad-acting metals which also form weak acidic oxides occupy the minima, which are much less sharp. That the size of the atomic sphere—be it sphere of influence or the outer spherical shell of electrons—is not a question of valency is quite clear. For the smallest atoms are those of oxygen of valency two and nitrogen of valency three or five, each having the atomic diameter 1·30 Å.U., whilst the univalent alkali metals have atomic domains varying from 3 to 4·75 Å.U., cæsium, the most electropositive element known, having this latter maximum atomic diameter. The atomic diameters are thus periodic functions of the atomic number. They will doubtless prove to be of great assistance in unravelling the structures of the more complex inorganic compounds.

The Law of Atomic Diameters accords well with the Lewis-Langmuir version of the atomic structure theory; for the electronegative elements which have the minima of atomic domain are precisely those which share electrons to complete the stable (inert gas) shell, having fewer electrons than correspond to the stable system. Indeed, it is apparently this sharing of electrons which causes the spheres to have smaller diameters than those of the electro-positive elements. On the other hand, as an electro-positive element does not share electrons in its outer shell with neighbouring

FIG. 9.
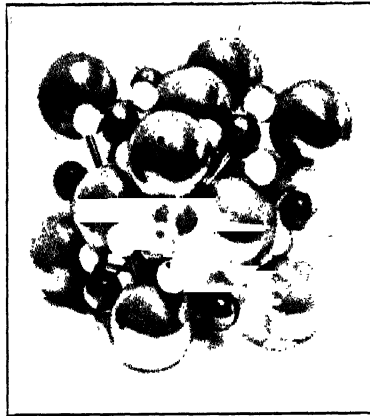
Model of Calcium Carbonate.

FIG. 10.
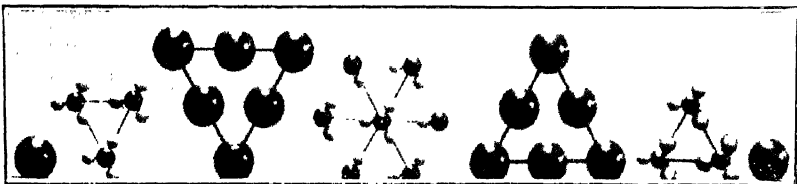
Dissected Model of Calcium Carbonate.

atoms, but has its active electron or electrons outside the stable shell, it occupies a greater space in the structure.   Perhaps the most instructive case referred to by Prof. Bragg, as affording both types of attachment in the same chemical compound, is that of calcite, $CaCO_3$, which is illustrated by models reproduced in Figs. 9 and 10, the latter showing the structure taken to pieces.   The calcium atoms, represented by the large spheres, have each a double positive charge, whilst the carbon and oxygen atoms of the CO_3 group together afford a corresponding double negative charge; the carbon and oxygen atoms of this group share electrons and are consequently knitted closer together (approximately at their atomic radial distance), so their spheres are smaller as shown by the model, the smallest being the oxygen atoms (lightly shaded in the figure).

Important confirmatory evidence of the law has been brought forward by Prof. A. O. Rankine [10] from the measurements of the viscosity of the four inert gases, and of oxygen, nitrogen, and the three halogens.   He has found that the nearest approach of the atoms of any one of these gaseous or vaporised elements to each other during a collision is only slightly greater than the atomic diameter of Bragg.   This is exactly what would be expected from thermally agitated atoms; a cushion or film of resiliency or repulsion between them (due probably to the electronic movements of Born and Landé) prevents absolute contact of the outer electronic shells on collision, otherwise attachment would occur.   Prof. W. L. Bragg has pointed out, moreover, that both the viscosity and the crystal structure results point to the same increase in the size of the atom as each successive electron shell is added, there being a definite increase in the dimensions of the outer electron shell in passing from one period to the next.

The Law of Progressive Crystal Structure in Isomorphous Series containing the Alkali Metals.

The remarkable outstanding size of the atoms of the alkali metals, as so clearly shown by their sharp maxima in the curve of atomic diameters, and also the considerable progressive increase in the dimensions of their shells as we pass from one to another (belonging to successive periods), explain and render still more important the two most prominent facts emanating from the writer's researches on the crystal-characters of the isomorphous sulphate, selenate and double salt series $R_2{\overset{S}{\underset{Se}{}}}O_4$ and $R_2M({\overset{S}{\underset{Se}{}}}O_4)_2,6H_2O$, in which R represents either potassium, rubidium, or cæsium.   The first fact is that in the double salt series these alkali metals exert a vastly

[10] A. O. Rankine, *Phil. Mag.*, 1920, [vi], **40**, 518; *A.*, 1920, ii, 679.

predominating influence in determining the properties of the crystals, their interchange causing a very definite change in the crystal angles and constants; whereas interchange of the dyad-acting M metals, which are near and almost on the minima of the curve of atomic diameters, has but a slight determinative effect on the angles, volume constants, and physical properties of the crystals. The second fact is that the specially marked changes due to interchange of the alkali metals, whether in the double salt series or in the alkali sulphates or selenates themselves, are definitely progressive, following the progression of the atomic numbers of the three alkali metals. Thus not only does the relatively very large size of the atoms of the three alkali metals (the cæsium atom being, as already mentioned, the largest of all atoms), and the consequent relative magnitude of the progressive difference in their sizes, cause the changes of crystallographic constants, both structural and physical, to be prominently marked, but it gives, in doing so, the maximum opportunity possible for any progressive character to reveal itself in these changes, corresponding to the addition of another electronic shell when we pass from potassium to rubidium and from the latter to cæsium. Hence, the choice of the salts of these metals—both the simple rhombic sulphates and selenates and the monoclinic hexahydrated double sulphates and double selenates—has proved a singularly suitable and fortunate one, and the Law of Progression of the Crystallographic Properties with Rise of Atomic Number of the Alkali Metals has been placed on the firmest possible basis.

Thus the Law of Atomic Diameters, together with the fundamental Law of Moseley—according to which the atomic number expresses the mass and positive charge on the atomic nucleus and also the number of the surrounding negative electrons—explains completely the results of the writer's investigations, which may be justly regarded as the natural consequence of these laws. Conversely also, Prof. Bragg may fairly consider that the writer's results support his law of atomic diameters.

It may perhaps be permitted to be stated in this Report, as the present moment marks the conclusion of a research which has occupied full thirty years, that the writer has now just completed the work on the last two groups of salts, the double selenates of the manganese and cadmium groups. Altogether seventy-five salts have been investigated, including also those in which R is ammonium and thallium, and also including a group of isomorphous double chromates, in investigating which the writer had the collaboration of Miss Mary W. Porter. The specially careful preparation of numerous crops of each of these seventy-five salts, the goniometry

of ten or more of the most perfect crystals of each of them, and the determination of their density (more than eight hundred crystals having been completely measured and five hundred density determinations carried out), the preparation of more than two thousand truly plane and correctly orientated surfaces with the very efficient aid of the cutting-and-grinding goniometer, in order to provide at least eight section-plates and six 60°-prisms of each substance, has alone been a formidable task, and fully explains the time over which the work has inevitably extended. It was felt to be essential to include every salt of these series which could be obtained in good crystals, and it is satisfactory to be able now to report that the conclusions are contributed unanimously, without any exception, by all the groups studied, which are nineteen in number. The crystal angles, the habits of the crystals, the volumes and edge-dimensions of the unit cells of the space-lattices, the dimensions and orientations of the optical ellipsoids, the molecular refraction constants, the thermal dilatations in all cases where it was possible to determine them, indeed the minutest details of the physical properties studied, have throughout exhibited the progression according to the atomic numbers of the three alkali metals ($K = 19$, $Rb = 37$, $Cs = 55$, a difference of eighteen at each step, corresponding to a whole Langmuir shell of electrons), the crystals of the rubidium salt invariably proving intermediate. The importance of the isostructure of the rubidium and ammonium salts, so clearly in all cases also revealed, has already been adequately referred to. In practically every property but refractive power, in which it is transcendently high, the thallium salt also stands close to the rubidium salt. It has been made very clear, moreover, that only the potassium, rubidium, and cæsium salts are " eutropic " (following the law of progression with atomic number of alkali metal), the ammonium and thallium salts being only generally isomorphous. The largest amount of change of angle for any replacement of one R-base by another has proved to be 2° 28′ (between potassium copper and cæsium copper selenates).

In two papers published during the year by Prof. P. Niggli of Zurich,[11] the editor of the now resuscitated *Zeitschrift für Kristallographie*, the connexion between crystal and atomic structure is discussed, and reference especially made to the writer's work. He points out that the homogeneity of crystal structure is not due to the arrangement of mere mass particles, but to the symmetry or structure of those particles themselves, the elementary atoms, and to the fields of force, orientated in character, which in consequence may be regarded as emanating from the atoms. He goes

[11] P. Niggli, *Z. Kryst. Min.*, 1921, **56**, 12, 167; *A.*, 1922, ii, 36.

I*

further in stating that from crystal structure that of the atoms building up the crystal ought to be elucidated. He turns largely to the determination of density in isomorphous series as an indication of the ranges, spheres of influence, or volumes of the atoms of the elements which by their mutual arrangement replace each other, and quotes the writer's determinations of the densities of the monoclinic hexahydrated series as typical and adequately accurate for his purpose, and as clearly proving the progressive growth of the sphere of influence of the atoms of the alkali metals as the atomic number increases. Niggli then analyses a considerable amount of the material in vols. I and II of Groth's "Chemische Krystallographie," with similar results, making allowances for less accurate experimental data, and finally arrives at relative volumes for the spheres of action of the atoms of many elements, and it is highly interesting that the corresponding relative diameters show the same regularities of periodicity as the atomic diameters in absolute measure of W. L. Bragg. This conclusion, moreover, was arrived at before the publication of Bragg's paper, so that it is doubly valuable as being an independent arrival at the Law of Atomic Diameters, largely from the work of the writer aided as far as possible by older measurements in other series, and especially confirmed as regards the morphological and volume constants by the excellent work of W. Muthmann on the permanganates and of T. V. Barker on the perchlorates of the alkalis.

In concluding this section of the Report, therefore, it may be pointed out how very satisfactorily the results of the investigations of so many different workers support, confirm, and amplify one another, so that we may now be sure that knowledge of real value and permanence has been arrived at during the year that has just closed.

Miscellaneous X-ray Results.

The Structure of Adularia and Moonstone.—The results of a useful investigation commenced at Cambridge by Mr. S. Kozu, concerning the structure of adularia and moonstone, and continued in Japan in collaboration with Y. Endo and M. Suzuki, are published in a new journal, *Science Reports of the Tohoku Imperial University, Sendai, Japan* (1921, Vol. I, No. 1, p. 1). Adularia and moonstone are supposed to be solid solutions of varying proportions of ortho-clase, albite, and anorthite felspars, moonstone being the variety of adularia which exhibits " schillerisation " (the display of a pearly, sub-metallic, or bronze-like lustre). The results indicate that adularia consists of a single space-lattice structure, a homogeneous solid solution, whilst moonstone has two different space-lattices of

like type, affording a double Laue radiogram, the two different substances being two kinds of solid solutions, both of monoclinic symmetry. On heating moonstone the two space-lattices approach each other and eventually become identical at 1060°, the lattice then being that of adularia. At about 1000° the schillerisation disappears. Hence this work has proved that schillerisation is not due to cavities and inclusions, as supposed, but to interference of ordinary light rays by the presence of two space-lattices alike in symmetry but quite distinct.

The Structure of " Liquid Crystals " has been studied by J. S. van der Lingen [12] by the Laue method of *X*-ray analysis, with the view of definitely testing whether these remarkable substances, so intimately associated with the name of Prof. Lehmann, are in reality endowed with a space-lattice structure, the criterion of a true crystal, as asserted by Vorländer, or are merely swarms of similarly orientated molecules, as supposed by Bose. *p*-Azoxyanisole, *p*-azoxyphenetole, anisaldazine, and active amyl cyanobenzylidene-aminocinnamate were produced in the so-called " liquid crystal " form in a strong magnetic field, and Laue *X*-radiograms taken of them. The result was definitely negative, no sign of a space-lattice being revealed. The regularity of structure producing double refraction and other optical effects simulative of crystals appears to be due merely to the similar orientation (parallelwise) of the flat elongated molecules themselves, the swarm theory of Bose being thus verified.

In a second memoir van der Linden [13] describes further experiments with the anisotropic liquid (the liquid crystal) form of *p*-azoxyanisole, in which a pattern of faint horizontal lines was obtained, apparently due to diffraction from parallel layers of lamellar molecules, a direct confirmation, it would seem, of Bose's swarms. In the writer's opinion Prof. Lehmann is to be congratulated on this result, although it is not in conformity with his earlier views. For his " liquid crystals " thus become an intermediate stage, of deeper interest than ever, between true liquids and true crystals.

The Structure of Alabandite, MnS, has been studied by R. W. G. Wyckoff.[14] The crystals belong to the hexakis tetrahedral class 31 of the cubic system, and *X*-ray analysis shows them to be constructed like rock-salt, but with some slight lack of symmetry in the lines of force about the atoms. It is thus different from zinc blende, ZnS. Magnesium oxide, MgO, afforded almost identical results, the sodium chloride structure being closely simulated.

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[12] J. S. van der Lingen, *J. Franklin Inst.*, 1921, **191**, 651; *A.*, ii, **438**.

[13] *Loc. cit.*, **192**, 511; *A.*, ii, 681.

[14] R. W. G. Wyckoff, *Amer. J. Sci.*, 1921, [v], **1**, 138; **2**, 239; *A.*, ii, 262, 700.

The Structure of the Ammonium Haloids has been investigated by Dr. Langmuir and G. Bartlett [15] at different temperatures. The high-temperature form of each proves to be constructed like sodium chloride, each atom being surrounded by six others. The ordinary-temperature forms of the chloride and bromide possess a centred cube structure, each atom having eight others around it. It is considered that the ammonium " ion " has tetrahedral symmetry, while the alkali metals and halogens have cubic " ions."

Colloidal Substances.—An interesting X-ray investigation of so-called colloids has been carried out by Scherrer.[16] Colloidal gold, the finest precipitated gold (that in the remarkable purple liquid which never deposits), was found to consist of minute crystal particles having the same face-centred cube structure as ordinary gold crystals, some of the particles being only $1·86 \times 10^{-7}$ cm. in diameter, so that only five cube-lattice edge-lengths were contained in each particle. Colloidal silver also proved to be crystalline, with a face-centred cube lattice. Silica likewise proved to be crystalline, and the only true colloid among the substances examined was gelatin, which showed no sign of crystal structure.

Metallic Elements.—A. W. Hull [17] has given a list during the year of further metallic elements investigated by him as regards their crystal structure by his powder method. The list is as follows, the dimensions of the cube edges or trigonal prism edges, and the axial ratio $a : c$ of the hexagonal metals, being also given.

Face-centred Cube Lattices.

Calcium	5·56	Å.U.
α-Cobalt	3·554	,,
Nickel	3·540	,,
Rhodium	3·820	,,
Palladium	3·950	,,
Iridium	3·805	,,
Platinum	3·930	,,

Centred Cube Lattices.

Chromium	2·895	Å.U.
Molybdenum	3·143	,,
Tantalum	3·272	,,

Hexagonal Close-packed Lattices.

			$a : c$
β-Cobalt	2·514	Å.U.	1 : 1·63
Cadmium	2·960	,,	1 : 1·89
Ruthenium	2·686	,,	1 : 1·59
Zinc	2·670	,,	1 : 1·86

The Structure of Ice has been studied by D. M. Dennison,[18] by producing a shower of minute crystals in a water-filled capillary tube, plunging it into liquid air, and using the Hull method. The results indicate the close-packed hexagonal lattice, consisting of two sets of interpenetrating triangular prisms, with edges 4·52 Å.U. and height 7·32 Å.U. The axial ratio found was $a : c = 1 : 1·62$,

[15] G. Bartlett and Irving Langmuir, *J. Amer. Chem. Soc.*, 1921, **43**, 84; *A.*, ii, 261.

[16] P. Scherrer, Zsigmondy's " Kolloidchemie," 3rd ed., p. 387.

[17] A. W. Hull, *Physical Rev.*, 1921, **17**, 42, 571.

[18] D. M. Dennison, *ibid.*, 1921, **16**, 20.

very near the theoretical 1·633 for a close-packed hexagonal arrangement of spheres. It may be remembered that Rinne found ice to be hexagonal bipyramidal, class 25 (that of apatite), with an axial ratio 1 : 1·678.

The Structure of the Silver Haloids has been determined by R. B. Wilsey,[19] in the laboratory of the Eastman Kodak Company, Rochester, N.Y., also by the powder method. The precipitates obtained by adding potassium chloride, bromide, or iodide solution to a solution of silver nitrate were employed, and the results prove the crystalline character of these precipitated silver salts. Also powdered fused silver bromide was used, with identical results. The chloride and bromide are constructed of simple cube lattices of the side dimensions 2·78 and 2·89 Å.U. respectively, one atom being associated with each point of the lattice. Silver iodide, however, gave results which corresponded with the diamond lattice, each side of the cube being 6·53 Å.U., one atom being ascribed to each point of the structure; each iodine atom appears to be at the centre of a tetrahedron the corners of which are occupied by four silver atoms, and each silver atom is surrounded by four iodine atoms in the same manner, the distance of the atomic centres being 2·83 Å.U. The silver bromide and chloride precipitated in photographic emulsions form minute distinct cubic crystals; the iodide similarly produced in these emulsions appears to be hexagonal. These forms had not been studied, but a promise of such an investigation by X-rays is given. The result should be interesting, as silver iodide crystallises at the ordinary temperature in the dihexagonal pyramidal class 26 of the hexagonal system, and becomes converted on heating to 146° into a cubic form.

The Crystal-structure of Antimony and Bismuth.—Prof. A. Ogg[20] has confirmed the conclusion of James and Tunstall that the unit rhomb of each of these metals contains eight atoms. The edge of the unit rhomb of antimony is 6·20 Å.U., the structure consisting of two interpenetrating face-centred rhombohedral lattices, and the shortest distance between the atoms is 2·92 Å.U. James and Tunstall made it 2·87 Å.U. The length of the edge of the unit rhomb of bismuth was found to be 6·52 Å.U. R. W. James,[21] in a further paper, gives it as 3·28 Å.U., the half of the value just quoted, and for the closest approach of two atomic centres 3·11 Å.U.

The Structure of Potassium Cyanide Crystals has been determined by P. A. Cooper[22] with small single crystals, and found to resemble that of potassium bromide, the CN acting as a whole like Br. But

[19] R. B. Wilsey, *Phil. Mag.*, 1921, [vi], **42**, 262; *A.*, ii, 548.

[20] A. Ogg, *ibid.*, 163; *A.*, ii, 513.   [21] R. W. James, *ibid.*, 193; *A.*, ii, 513.

[22] P. A. Cooper, *Nature*, 1921, **107**, 745.

no definite evidence was obtained as to the disposition of the atoms of carbon and nitrogen.

The Diamond.

Three papers of general interest concerning the diamond have appeared during the year 1921. One embodies a communication to the Mineralogical Society by Dr. J. R. Sutton,[23] Director of the Kimberley Observatory, S. Africa, who showed that diamond crystallises readily on garnet, iron pyrites, olivine, and ilmenite ($FeTiO_3$). These minerals are frequent inclusions in diamond, as are also graphite, bort, and diamond itself of unconformable orientation. So common are diamond inclusions (either fragments or complete crystals) in the diamonds found at Bullfontein that they impart a specific reputation to these "stones," for white spots, cross-grain, and "knots." It is these various inclusions which set up strain, and even fracture, in the enclosing diamond, and most diamonds found broken owe their rupture to this cause. Dr. Sutton entirely discredits the stories of bursting and exploding natural diamonds, and in a long experience has never known an authentic case. Such strain as there is in a diamond, revealed in the dark field of the polariscope, Dr. Sutton attributes entirely to inclusions, the thermal dilatation of which is different from that of the diamond. Artificial diamonds, however, do explode from strain. The late Sir William Crookes in his fascinating book "Diamonds" (page 120) describes how such an artificial diamond exploded on a microscope slide in his laboratory during the night, the diamond having been produced under great pressure.

A second paper by F. Fischer [24] deals with the artificial preparation of diamonds, and it is shown that under other than abnormally high pressures the separation of carbon as diamond (a non-conductor of electricity) can only occur below 700°, and that otherwise it appears as graphite (a conductor). The small size of the hitherto produced artificial diamonds he attributes to this fact, for at 700° the iron containing the carbon in solution has already solidified, so that the carbon could separate only in minute crystals. He suggests that larger diamonds would probably be produced if a substance could be found in which carbon is soluble and which is still molten at 700°.

The third paper concerns the compressibility of the diamond, which has been studied by L. H. Adams,[25] and found to be the lowest on record, namely, $0·16 \times 10^{-6}$ per megabar (a megabar =

[23] J. R. Sutton, *Min. Mag.*, 1921, **19**, 208.

[24] F. Fischer, *Brennstoff-Chem.*, 1921, **2**, 9; *A.*, ii, 111.

[25] L. H. Adams, *J. Washington Acad. Sci.*, 1921, **11**, 45.

0·987 atmosphere), within the range of pressure from 4,000 to 10,000 megabars. The difference from graphite is immense, the value for graphite having been shown by Prof. T. W. Richards to be 3×10^{-6}, and that of steel to be $0·6 \times 10^{-6}$. Thus we have one more property added to those for which the diamond 'holds the record.

Concluding Remarks.

This Report has already reached the allotted span, and a number of other valuable contributions to the work of the year 1921 can only be mentioned. Dr. H. H. Thomas and Mr. A. F. Hallimond [26] have devised a useful direct-vision refractometer for liquids, which also serves the special purpose of preparing a liquid mixture of any required definite refractive index, a most desirable object in modern optical crystallography. Miss Mary W. Porter [27] has extended the research mentioned in the last Report, which she carried out in collaboration with Mr. T. V. Barker, by describing crystallographically a number of pyridine and picoline derivatives which might have been expected to show some morphotropic regularities. But organic radicle replacements prove to cause very great (indeed often entire) change of crystalline form, indicating how very sensitive crystal structure is to change of chemical composition.

Dr. Harold Hilton [28] has contributed two papers of mathematical and geometrical interest, one regarding the determination of optic axes from extinction angles, and the other concerning the vibrations of a crystalline medium. Both subjects are treated in a masterly manner, and the latter paper gives food for much thought, at a time when atomic structure is proving to be at the root of molecular movements and the building up of a crystal edifice. A new mineral, a basic copper phosphate, of peacock-blue colour by reflected light and greenish-blue by transmitted light, is described by Dr. A. Hutchinson (to whom hearty congratulations are due on his election as the new President of the Mineralogical Society) and Mr. A. M. Macgregor.[29] It proves to have the composition $2Cu_3(PO_4)_2,7Cu(OH)_2$, and was discovered in Northern Rhodesia.

Dr. L. J. Spencer [30] has published two papers. The earlier one deals with a substance which was described in the year 1879 by C. O. Trechman as an orthorhombic form of metallic tin and termed by him β-tin. It is now shown to be not tin but stannous sulphide,

[26] H. H. Thomas and A. F. Hallimond, *Min. Mag.*, 1921, **19**, 124.

[27] Miss Mary W. Porter, *T.*, 1921, **119**, 1769.

[28] H. Hilton, *Min. Mag.*, 1921, **19**, 233; *Phil. Mag.*, 1921, [vi], **42**, 148.

[29] A. Hutchinson and A. M. Macgregor, *Min. Mag.*, 1921, **19**, 225; *A.*, ii, 701.

[30] L. J. Spencer, *ibid.*, 113, 263; *A.*, ii, 266.

the orthorhombic crystals of which are often produced in tin smelting. Tin is thus not trimorphous, but only dimorphous, ordinary white tin being tetragonal, and "grey tin" (tin pest) cubic. The second memoir is a fascinating essay, with numerous beautiful illustrations, on curvature in crystals. Many of the most remarkable examples of curved crystals in the British Museum collection are described and portrayed. The paper is not only pleasantly readable, but forms an admirably concise summary of the types of crystal distortion and contortion.

To Dr. Spencer it is largely due that the new venture of the Mineralogical Society, the publication of *Mineralogical Abstracts*, commenced in March, 1920, has been carried successfully through eight numbers and is now so nearly up to date that nineteen of the memoirs published in the past year, 1921, have been dealt with. The value of these abstracts is now assured, and they are most heartily welcomed. To the December number of the *Mineralogical Magazine* Dr. Spencer also contributes a considerable number of valuable biographical notices, with portraits, of lately deceased crystallographers and mineralogists, including Profs. Fedorov, von Lang, and Voigt, together with an index to all such notices which have appeared in the *Magazine* since its inception in 1876.

In the March, 1921, number of the *Magazine* appears an important Report, of the Committee on British Petrographic Nomenclature, of which Committee, jointly appointed by the Geological and Mineralogical Societies, Prof. W. W. Watts was chairman and Lt.-Col. Campbell Smith was secretary. The recommendations will do much to bring order into the somewhat chaotic state of this nomenclature.

During the year 1921 the Mineralogical Society has lost one who was universally regarded as the "father" of the society, its president during the years 1885 to 1888 and its general secretary for the succeeding twenty-one years, Sir Lazarus Fletcher. His name is happily perpetuated in the "Fletcher Indicatrix," the ellipsoid now so conveniently used to express the optical properties of crystals. An admirable biographical notice by Sir Henry Miers, with portrait, appears in the June (1921) number of the *Mineralogical Magazine*, and in this same number, by a singular chance, is published also Sir Lazarus Fletcher's last paper, a memoir written with all his accustomed thoroughness, on "The Crumlin (Co. Antrim) Meteorite."

During the meeting of Science Masters at Oxford in January, 1921, some interesting demonstrations were given by Mr. T. V. Barker at the Mineralogical Department of the University, on "The Study of Crystals in Schools," and a very useful pamphlet

of " Practical Suggestions " for this study has been published by the Holywell Press.

During the year 1921 three important books have appeared. Of two bearing the same title, " Lehrbuch der Mineralogie," one is a new book by Prof. P. Niggli [31] of Zurich, already referred to as the new editor of the resuscitated *Zeitschrift für Kristallographie,* and the other, edited by Prof. F. Becke [32] of Vienna, is the 8th edition of the text-book of Prof. Gustav Tschermak. The third is a new book by Prof. P. von Groth,[33] an attempt to combine in abbreviated form the characters of his well-known " Physikalische Krystallographie " and of his large (5-volume) " Chemische Krystallographie."

By the time this Report appears it is probable that a second and very much enlarged edition of the writer's " Crystallography and Practical Crystal Measurement " will have been published. The immense amount of research, including the whole of the X-ray work, carried out since the appearance of the first edition in 1911, and the desirability of acceding to the many expressed wishes that the book should be made more fully to cover the whole subject, have caused it to be extended to two volumes.

It will be evident to all who read this Report how very considerably the crystallographic investigations of the past year, so large a proportion of which are British, have contributed to the very basis of Chemistry, the unravelling of the nature of the chemical atom. There is no longer any necessity for a crystallographer to plead for more attention to his subject, its value is now most clearly evident to all. The realm of Organic Chemistry is now also entered, and indeed no one can say how far the new methods of attack by X-rays will take us, the possibilities being immense. Perhaps, however, the most encouraging fact is that all this recent research has permanently confirmed the principles on which crystallographers of late years have built up their science. For, as the writer states in the preface to the new edition of his book, " not one single conclusion or principle, presented in the first edition, has been shown to be invalid or incorrect."

<div align="right">A. E. H. TUTTON.</div>

[31] P. Niggli, " Lehrbuch der Mineralogie," 1920, Gebrüder Borntraeger, Berlin.

[32] G. Tschermak and F. Becke, *ibid.*, 8th edition, 1921, A. Hölder, Vienna and Leipzig.

[33] P. Groth, " Elemente der phys. und chem. Krystallographie," 1921, R. Oldenbourg, Munich and Berlin.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
A.	Abstracts in Journal of the Chemical Society.*
Amer. Chem. J. . . .	American Chemical Journal.
Amer. J. Bot. . . .	American Journal of Botany.
Amer. J. Dis. Child. . .	American Journal of Diseases of Children.
Amer. J. Hygiene . .	American Journal of Hygiene.
Amer. J. Physiol. . .	American Journal of Physiology.
Amer. J. Sci. . . .	American Journal of Science.
Amer. Min. . . .	American Mineralogist.
Anal. Assoc. Quím. Argentina	Anales de la Asociacíon Química Argentina.
Anal. Fis. Quím. . .	Anales de la Sociedad Espanõla Física y Química.
Analyst . . : .	The Analyst.
Annalen . . .	Justus Liebig's Annalen der Chemie.
Ann. Appl. Biol. . .	Annals of Applied Biology.
Ann. Bot. . . .	Annals of Botany.
Ann. Chim. anal. . .	Annales de Chimie analytique appliquée à l'Industries à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Physik . . .	Annalen der Physik.
Ann. Phytopath. Soc. Japan.	Annals of the Phytopathic Society, Japan.
Ann. Report . . .	Annual Reports of the Chemical Society.
Arch. exp. Path. Pharm. .	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim. Sci. .	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Pharm. . . .	Archiv der Pharmazie.
Arch. Schiffs u. Tropenhygiene	Archiv Schiffs-und Tropen-Hygiene.
Arch. Suikerindus. Ned. Ind.	Archiv voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv. Kem. Min. Geol. .	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J. . . .	Astrophysical Journal.
Atti R. Accad. Lincei . .	Atti della Reale Accademia Nazionale dei Lincei.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
Ber. Deut. bot. Ges. . .	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges. .	Berichte der Deutschen pharmazeutischen Gesellschaft.
Berl. Klin. Wochenschr. .	Berliner Klinische Wochenschrift.
Bied. Zentr. . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. J. . . .	The Biochemical Journal.
Biochem. Z. . . .	Biochemische Zeitschrift.
Boll. Chim. farm . .	Bolletino Chimico farmaceutico.
Brennstoff-Chem. . .	Brennstoff Chemie.
Brit. Assoc. Rep. . .	Report of the British Association for the Advancement of Science.
Brit. Med. J. . . .	British Medical Journal.
Brit. Pat. . . .	British Patent.
Bul. Soc. Chim. Românía .	Buletinul Societătei de Chimie din Românía.
Bull. Acad. Sci. Cracovie .	Bulletin International-Académie des Sciences de Cracovie.

ABBREVIATED TITLE.	JOURNAL.
Bull. Bur. Biotechn.	Bulletin of the Bureau of Biotechnology.
Bull. Johns Hopkins Hosp.	Bulletin of the Johns Hopkins Hospital.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim. Biol.	Bulletin de la Société de Chimie biologique.
Canada Med. Assoc. J.	Journal of the Canadian Medical Association.
Chem. Listy	Chemické Listy pro Vědu a Průmysl.
Chem. and Met. Eng.	Chemical and Metallurgical Engineering.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Ztg.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Chim. et Ind.	Chimie et Industrie.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
D.R.-P.	Deutsches Reichs-Patent.
Fermentforsch.	Fermentforschung.
Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh.	Geologiska Föreningens i Stockholm Förhandlingar.
Giorn. Chim. Ind. Appl.	Giornale di Chimica Industriale ed Applicata.
Helv. Chim. Acta	Helvetica Chimica Acta.
Internat. Mitt. Bodenkunde.	Internationale Mitteilungen für Bodenkunde.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Assoc. Off. Agr. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Bact.	Journal of Bacteriology.
J. Biochem. (Japan)	Journal of Biochemistry (Japan).
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Ind. Japan (or Tokyo)	Journal of Chemical Industry, Japan.
J. Chem. Soc. Japan.	Journal of the Chemical Society of Japan.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Agric. Hokaido	Journal of the College of Agriculture, Hokaido.
J. Exper. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Soc. Japan.	Journal of the Pharmaceutical Society of Japan.
J. Physical Chem.	Journal of Physical Chemistry.
J. Phys. Radium	Journal de Physique et le Radium.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kentucky Exp. Sta. Bul.	Kentucky Experimental Station Bulletin.
Koll. Chem. Beihefte.	Kolloidchemische Beihefte.
Kolloid Z.	Kolloid Zeitschrift.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.

ABBREVIATED TITLE	JOURNAL.
Landw. Versuchs-Stat.	Die Landwirtschaftlichen Versuchs-Stationen.
Medd. K. Ve'en-kapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Michigan Agric. Exp. Sta.	Michigan Experimental Station Bulletin.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. Sci.	Moniteur Scientifique.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
Oesterr. Chem. Ztg.	Oesterreichische Chemiker-Zeitung.
Oregon Agric. Exp. Sta. Bull.	Oregon Experimental Station Bulletin.
P.	Proceedings of the Chemical Society.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Proc. Amer. Phil Soc.	Proceedings of the American Philosophical Society.
Proc. Cam. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society of Experimental Biology and Medicine.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rev. Mét.	Revue de Métallurgie.
Schweiz. Apoth. Ztg.	Schweizerische Apotheker Zeitung.
Sci. Proc. R. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften Wien.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Soil Sci.	Soil Science.
Svensk. Kem. Tidskr.	Svensk Kemist Tidskrift.
T.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
U. S. Geol. Survey Prof. Paper	United States Geological Survey Professional Paper.
U.S. Pat.	United States Patent.
Ver. Deut. Physikal. Ges.	Verhandlungen der deutschen physikalischen Gesellschaft.
Wiss. Veröffentl. Siemens Konzern	Wissenschaftliche Veröffentlichungen aus dem Siemens Konzern.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. Elektrochem.	Zeitschrift für Elektrochemie.

ABBREVIATED TITLE.	JOURNAL.
Z. ges. Schiess-u. Spreng-stoffw.	Zeitschrift für das gesammte Schiess-und Spreng-stoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Nahr.-Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

Spectra of Hydrogen and Helium.

THE line spectrum attributed to neutral helium contains 105 lines, forty of which are accounted for by a formula [1] derived on the assumption that the mutual perturbation of the electrons is negligible. It is anticipated that the majority of the remaining lines will be found to fit the formula, and the conclusion is drawn that the field of force of the bound electrons is entirely engaged by the nucleus. In a criticism [2] of this interpretation of the spectrum, it is suggested that the agreement between the observed and calculated frequencies is largely fortuitous.

The band spectrum of helium has been further investigated.[3] Fowler found that the heads of some of the bands in this spectrum conform to the ordinary law for line series. It is now shown that three of the remaining bands, including the strongest in the spectrum, can be deduced from the recently developed quantum theory of band spectra. The three bands in question are supposed to be emitted by a molecule which is undergoing simultaneous changes in its rotational and internal energies, and, in agreement with theory, each band contains three main series of lines represented by similar parabolic formulæ and characterised by a common fundamental frequency which is not simply related to the "head" of the band. This work is of general interest on account of the support it affords to the view that diatomic molecules of helium exist under the conditions which prevail in the discharge tube.

Although the origin of some parts of the secondary spectrum of hydrogen is probably analogous to that of the helium bands, its structure is still obscure. Electric discharge through vacuum tubes is the only known means by which this spectrum is excited

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[1] L. Silberstein, *Nature*, 1922, **110**, 247; *A.*, ii, 674.
[2] C. V. Raman, *ibid.*, 700; *A.*, ii, 803.
[3] W. E. Curtis, *Proc. Roy. Soc.*, 1922, [*A*], **101**, 38; *A.*, ii, 330.

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and its intensity, relative to that of the Balmer lines, increases with the purity of the hydrogen. The Doppler effect, to which the spectral broadening of monochromatic radiation is to be attributed, affords a means of determining the mass of the radiating particle with the aid of Rayleigh's formula, $\alpha_\lambda = k\lambda\sqrt{T/M}$, in which α_λ is the half-width of the line of wave-length λ, M is the mass of the radiator, and T the absolute temperature. The older methods of determining the "half-width" fail to give satisfactory results in dealing with such closely packed lines as those in the secondary spectrum of hydrogen, of which 1200 have been measured at an average interval of less than 3 Å. A new method [4] has, however, been described which depends on the relation between the width of the photographic image of the line under investigation and the intensity of the radiating source. If the intensity is cut down to a known fraction, whilst the time of exposure remains the same, it can be shown that for an apparatus of given dispersive power, the difference between the widths of the images is determined by the "half-width" of the line examined. Such "half-width" data indicate definitely that the hydrogen molecule is the source of the secondary spectrum of hydrogen. The same conclusion has been reached by R. W. Wood,[5] who, by eliminating the secondary spectrum and the faint continuous background, and by the use of long exposures, has increased the number of observed Balmer lines to twenty.

Fluorescence of Mercury Vapour.

The fluorescence of mercury vapour is only exhibited [6] when the vapour has been freshly distilled from liquid mercury at temperatures above 150°. It is suggested that such vapour contains aggregates of mercury atoms as well as the normal monatomic molecules and that the former are responsible for the fluorescence. The continuous portion of the fluorescence spectrum has also been produced [7] by the electrical excitation of mercury vapour. The spectrum is only obtained within certain limiting temperatures and when the density of the exciting current is low.

Specific Heats of Gases.

Although the advances recently made in the interpretation of the specific heats of solids involve the acceptance of views which

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[4] T. R. Merton and S. Barratt, *Phil. Trans.*, 1922, [A], **222**, 369; *A.*, ii, 461.

[5] *Phil. Mag.*, 1922, [vi], **44**, 538; *A.*, ii, 673.

[6] J. S. van der Lingen and R. W. Wood, *Astrophys. J.*, 1921, **54**, 148; *A.*, ii, 245.

[7] C. D. Child, *ibid.*, 1922, **55**, 329; *A.*, ii, 676.

are incompatible with the equipartition principle, there is an evident disinclination to discard this principle in the theoretical treatment of the specific heats of gases.

As the simplest member of the group of polyatomic gases, the behaviour of hydrogen is of peculiar interest in this connexion. At very low temperatures, its specific heat is constant and it behaves as a monatomic gas. At higher temperatures, the specific heat increases with the temperature, but the relation between the heat capacity and the temperature is not of a simple kind.

On the assumption that collisions between the gaseous molecules give rise to additional degrees of freedom when the velocities of the colliding molecules exceed a certain critical value, the total energy of the gas will be the sum of the energies of the fraction for which the collision velocities are less than the critical value, and of the fraction for which the velocities of collision are greater than this. By assigning an appropriate value to the critical velocity, and assuming that the molecules in the two groups have three and five degrees of freedom, respectively, it has been shown [8] that the observed variation in the molecular heat of hydrogen at temperatures below 0° can be accounted for in a fairly satisfactory manner.

Bjerrum, Krüger, and Eucken had previously shown that the quantum theory affords a promising basis for the interpretation of the experimental data, although the formulæ suggested by these authors show deviations from the observed numbers which are greater than the errors of experiment.

A more recent investigation [9] of the problem shows that the entire range of data can be represented very satisfactorily by the formula

$$C_v = \tfrac{3}{2}R + 1{\cdot}13R\mathrm{f}(\nu_1) + R\mathrm{F}(\nu_2),$$

in which R is the gas constant, f and F are abbreviations for the Planck-Einstein and the Nernst-Lindemann functions, respectively, and $\nu_1 = 10{\cdot}06 \times 10^{12}$, $\nu_2 = 1{\cdot}84 \times 10^{14}$ are characteristic rotation and vibration frequencies calculated from numerical data relating to Bohr's model of the hydrogen molecule. The first term gives the energy increment per degree at low temperatures and has reference solely to translational energy; since the corresponding quanta are very small, the energy exchange is practically continuous and in agreement with the equipartition theory. Above 60° abs., the influence of the rotational quanta, represented by the second term, begins to be appreciable and causes C_v to rise to about $\tfrac{5}{2}R$, at which point the vibration quantum comes into play and

[8] G. W. Todd, *Phil. Mag.*, 1920, [vi], **40**, 357; *A.*, 1920, ii, 585.

[9] C. K. Ingold and (Miss) E. H. Usherwood, *T.*, 1922, **121**, 2286.

causes a further rise in the molecular heat as the temperature increases. The introduction of the factor 1·13 in the second term represents an empirical adjustment, in regard to which it is tentatively suggested that the quantity $0·13Rf(\nu_1)$ may correspond with some form of potential energy which is associated with precessional motion.

In reproducing the experimental data, the above formula is a distinct improvement on that proposed by F. H. MacDougall,[10] who also employs Bohr model frequencies but, on the other hand, assumes that the hydrogen molecule has three degrees of rotational freedom and uses Planck-Einstein functions in evaluating the rotational and vibrational energy terms.

The successful application of the notions associated with the quantum theory in so many different directions leads rather naturally to the expectation that this will ultimately provide the key to the theoretical treatment of the problem of the energies of gaseous molecules, but so long as the agreement between theory and experiment depends in the first instance on the arbitrary choice of the number of the degrees of freedom and of the nature of the operating functions, and subsequently on the empirical adjustment of the formulæ so derived, it is perhaps not difficult to understand why there should be a certain reluctance to ignore the equipartition principle in dealing with this problem.

With the object of providing accurate data for the theoretical investigation of the problem, an improved adiabatic method has been developed [11] for the determination of the specific heat ratio, and measurements [12] have been made of the specific heats of a number of gases.

The specific heat of a gas has an abnormally high value if with rise of temperature it dissociates or undergoes some intramolecular change which is accompanied by heat absorption. The value of the molecular heat ratio $\gamma = (C_v + R)/C_v$ will under these circumstances be less than the normal value. These considerations have been applied [13] to detect and measure the supposed tautomeric equilibrium represented by HCN $\rightleftharpoons$ HNC in gaseous hydrogen cyanide. The heat absorbed in the transformation of formonitrile into carbylamine is about 7000 calories per gram-molecule, a value large enough to ensure the detection of the

[10] J. Amer. Chem. Soc., 1921, **43**, 23; A., 1921, ii, 238; see also Ann. Rep., 1921, 1.

[11] J. R. Partington, Proc. Roy. Soc., 1921, [A], **100**, 27; A., 1921, ii, 621.

[12] J. R. Partington and H. J. Cant, Phil. Mag., 1922, [vi], **43**, 369; A., ii, 191.

[13] (Miss) E. H. Usherwood, T., 1922, **121**, 1604.

tautomeric equilibrium, even if one of the tautomeric forms is present at the temperature of the measurements only in very small proportion. The experimental data actually show that gaseous hydrogen cyanide is a mixture consisting mainly of HCN in equilibrium with a small amount (not more than a few tenths of one per cent.) of the isomeric form, HNC.

Viscosity of Gases and Molecular Configuration.

Measurements of the viscosity of gases provide data which would appear to throw some light on the arrangement of the atoms in the molecules of which they form part.

The viscosity depends on the frequency of molecular collisions, which in its turn is determined by the effective cross-sectional areas which are presented by the molecules as targets. The average area presented by a molecule in all possible orientations is known as the " mean collision area " and this is calculated from the viscosity in the same way as the cross-sectional area of a molecule which is assumed to be spherical.

When such " mean collision areas " are considered [14] in reference to modern views of atomic structure, and to the part which, according to the Lewis-Langmuir theory, is played by the valency electrons in the combination of the elements to form compounds, it is apparent that this magnitude will depend on the molecular configuration.

It seems natural to suppose that elements which have the same number of electron rings and which differ only in regard to the degree of development of the outermost ring will show comparatively slight variations in atomic diameter, provided of course that the number of such valency electrons is not too small. Contiguous elements on the right-hand side of the periodic table form such a group. It has in fact been shown [15] by X-ray measurements that the domains occupied by the atoms of such contiguous elements are the same within narrow limits, and other evidence [16] pointing in the same direction is available.

According to the Lewis-Langmuir theory, the hydrogen compounds of the elements chlorine, sulphur, phosphorus, and silicon [17] have an outer ring structure which is essentially identical with the outer ring structure of the inert element argon. The outer rings of these elements are indeed completed by the entry of one, two, three, and four electrons, respectively, from the corresponding

[14] A. O. Rankine, *Trans. Faraday Soc.*, 1922, **17**, 719; *A.*, ii, 635.

[15] W. L. Bragg, *Phil. Mag.*, 1920, [vi], **40**, 169; *A.*, 1920, ii, 537.

[16] A. O. Rankine, *Proc. Roy. Soc.*, 1921, [4], **98**, 360; *A.*, 1921, ii, 192.

[17] A. O. Rankine and C. J. Smith, *Proc. Phys. Soc.*, 1922, **34**, 181; *A.*, ii, 709.

number of hydrogen atoms. Differences in size and shape may therefore be attributed to the hydrogen nuclei which are associated with these electrons in the respective hydrogen compounds.

The " mean collision areas " of such compounds compared with that of argon are shown in the following series :

	A.	HCl.	H_2S.	PH_3.	SiH_4.
Mean collision area	1·00	1·04	1·19	1·41	1·53
Difference		0·04	0·15	0·22	0·12

On the assumption that the hydrogen nuclei may be regarded as forming protuberances on the spherical argon atom, the above data point to the conclusion that the distance between the hydrogen nuclei and the nucleus of the central atom increases with increase in the number of hydrogen atoms in the molecule. The reason for this is possibly to be found in the mutual repulsion of the hydrogen nuclei.

The difference figures show that the increase in the " mean collision area " due to a hydrogen nucleus reaches a maximum when the third nucleus is attached, the effect of the fourth being distinctly smaller. It is to be noted, however, that in the case of phosphine, and still more in the case of silicane, the effect of the repulsion will be to some extent obscured, in so far as the viscosity is concerned, by the overlapping of the nuclear prominences which occur in certain orientations of the molecule.

The viscosity data for other groups of related compounds have also been interpreted [18] in the light of the Lewis-Langmuir theory. According to this, the molecule of carbon dioxide is externally equivalent to three linked atoms of neon with their centres disposed linearly. If one of the external neon atoms is replaced by an atom of argon, an electronic configuration is obtained which is equivalent to that of carbon oxysulphide. The " mean collision areas " calculated from the viscosities of carbon dioxide and carbon oxysulphide are in good agreement with this view of their molecular structure.

Limiting Densities of Gases.

The compressibilities of oxygen, hydrogen, carbon dioxide,[19] and ethylene [20] have been measured at low pressures. The values of $(pv)_0/(pv)_1$ lead to the following values for the atomic weights : H = 1·0077, C = 11·998 (from carbon dioxide), C = 12·000 (from ethylene).

Wohl's equation of condition has been applied [21] to the deter-

[18] A. O. Rankine, *Phil. Mag.*, 1922, [vi], **44**, 292; *A.*, ii, 704.
[19] P. A. Guye and T. Batuecas, *Helv. Chim. Acta*, 1922, **5**, 532; *A.*, ii, 617.
[20] T. Batuecas, *ibid.*, 544; *A.*, ii, 618.
[21] *Z. physikal. Chem.*, 1921, **99**, 207; *A.*, ii, 117.

mination of the limiting density (D_0) of a number of gases, the relation between this and the normal density (D) being given by the equation $D_0/D = 1 + \dfrac{t}{15p_c}(1 - 6\cdot4t^2)$, where $t = T_c/T$ and p_c is the critical pressure. The molecular weights corresponding with the limiting densities are in close agreement with those derived from the formula of D. Berthelot, which is of the same form as that given above and differs from it only in the values of the numerical constants involved.

Equations of Condition.

Attention has been recently directed to the exactitude with which the observed relations between the pressure, volume, and temperature of fluids are reproduced by the equation of A. Wohl.[21a] This equation may be written in the form,

$$p = \frac{RT}{v-b} - \frac{a}{Tv(v-b)} + \frac{c}{T^2v^3},$$

in which the second term on the right represents the diminution of pressure due to the attractive forces and the third term represents the increase due to the repulsive forces which come into play at high pressures as a result of the rotational movements of the molecules.

The equation is of the fourth degree in regard to v and apparently contains four constants, but on the assumption that the four roots are identical in the critical condition, it may be shown that the four constants can be expressed in terms of the critical data, or, more conveniently from the experimental point of view, in terms of the specific constants p_c and T_c, and the general constant R. Since three independent constants only are involved, the Wohl equation can be transformed into a general reduced equation of condition.

In comparing the Wohl equation with that of van der Waals, it should be noted that although the latter expresses qualitatively the relations between the gaseous and liquid states, it can only be regarded as a very approximate quantitative statement of the behaviour of fluids. Wohl's equation, however, represents the experimental results with very considerable accuracy over an extended range. Furthermore, this equation reproduces the experimental values of v_c and $\dfrac{RT_c}{p_c v_c}$, and since at low pressures it is practically identical with the equation of D. Berthelot, it possesses all the advantages of the latter in this region.

[21a] Z. physikal. Chem., 1914, 87, 1; A., 1914, ii, 430.

In a series of later papers,[22] the range of applicability of the equation has been considered in greater detail. As an equation of condition of considerable accuracy, it appears to be limited to conditions in which the volume is not much less than the critical volume, and it would seem that the influence of temperature on the repulsive forces between the molecules varies from one substance to another. The equation has been criticised by R. Wegscheider [23] on the ground that it entirely fails to accord with the observed compressibility of liquids at low temperatures and high pressures.

The data obtained by Amagat and by Bridgman in their investigations on the compressibility of liquids at high pressures can be satisfactorily represented by a formula [24] based on the differential equation $\dfrac{1}{v_0}\left(\dfrac{dv}{dp}\right)_T = -\dfrac{a}{K+p}$, in which the volume change dv is measured with reference to the volume v_0 (corresponding with $p = 0$), a is a specific constant, and K, the internal pressure, is a linear function of $t = T_c/T$.

The equation $(p + a/v^2)(v - b) = RT\Big/\left(1 + \dfrac{\psi^2}{T^2}\right)$, in which ψ is a characteristic temperature, is said [25] to accord very well with the behaviour of substances in the gaseous state. At the same time, it yields values for the entropy, internal energy, and heat capacity which are consistent with Nernst's heat theorem.

Vapour Pressures.

The formulæ commonly employed to express the dependence of the vapour pressure of liquids on the temperature are derived from the Clausius-Clapeyron equation by incorporating the simple gas laws and assuming that the heat of vaporisation can be expressed either as a linear function or as a quadratic function of the temperature. The former assumption leads to the Kirchhoff-Hertz formula, whilst the latter gives the formula usually associated with the name of Nernst. These formulæ involve respectively three and four constants, the values of which may be determined empirically from the observed vapour pressures at three or four different temperatures. For a wider range of temperature, the Nernst formula is in general to be preferred, although in view of the assumed validity of the simple gas laws it may be seriously doubted whether the use of the four-term equation can be justified except for comparatively low vapour pressures.

[22] A. Wohl, *Z. physikal. Chem.*, 1921, **99**, 207, 226, 234; *A.*, ii, 117.
[23] *Ibid.*, 361; *A.*, ii, 192.
[24] H. Carl, *ibid.*, 1922, **101**, 238; *A.*, ii, 477; see also Wohl, *loc. cit.*
[25] W. P. Boynton and A. Bramley, *Physical Rev.*, 1922, **20**, 46.

Simpler formulæ covering a wide range of temperatures have been recently put forward by F. A. Henglein.[26] Denoting by T_1 and T_2 the temperatures at which two different liquids, L_1 and L_2, have the same vapour pressure, this author has shown that the thermodynamic equation of Clausius-Clapeyron leads to the isobaric temperature formula

$$\log T_1 = a \log T_2 + b \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which a and b are constants. Since the coefficient a is the ratio of the values of $\lambda/p(v - v')$ for the liquids L_2 and L_1, it is approximately equal to the ratio of the Trouton numbers, and since the Trouton numbers for normal liquids are nearly identical, it follows from formula (1) that such liquids should obey the simple empirical Ramsay-Young rule,

$$T_1/T_2 = k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Equation (1) may be written in the form

$$T_1 = C \cdot T_2{}^a \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\log C = b$, and just as the isobaric temperature rule of Ramsay and Young corresponds with the vapour pressure formula

$$\log p = -\frac{k}{T} + C_1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which C_1 has the same value for all substances, it is evident that equation (3) corresponds with the vapour pressure formula

$$\log p = -\frac{k}{T^n} + C_2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which k and n are specific constants and C_2 is a general constant having the same value for all substances.[27] The value of n is given by $K \dfrac{\lambda}{p(v - v')}$, where K is independent of the nature of the substance and λ, v, and v' are measured at atmospheric pressure. Having regard to the simple character of this formula, the range of its validity is surprisingly large. It applies equally well to normal and associated liquids, and its general utility has been demonstrated by applying it to sublimation pressures and dissociation pressures. The agreement may be illustrated by a comparison of the observed and calculated vapour pressures of mercury between 0° and 800°.

T (abs.)	273°	383°	473°	553°	633°	723°	823°	1073°.
p (obs.)	0·00019	0·013	18·25	158·4	806	4·25	50·0	102.
p (cal.)	0·000198	0·0132	17·6	159·0	811	4·29	49·8	99·5.

[26] *Z. Elektrochem.*, 1920, **26**, 431; *A.*, 1920, ii, 732.

[27] F. A. Henglein, *Z. physikal. Chem.*, 1921, **98**, 1; *A.*, ii, 118.

The pressures up to 633° are recorded in mm.; above this temperature, in atmospheres.

With the object of testing the applicability of the various vapour pressure formulæ, accurate measurements [28] have recently been made of the vapour pressure of lead by determining its boiling point in an atmosphere of nitrogen. The range covered extends from 920° (1·49 mm.) to 1340° (90·3 mm.). Under these low pressures, it may be assumed that the saturated monatomic vapour does not deviate appreciably from the simple gas laws.

It is found that the Nernst formula does not reproduce the experimental results within the limits of the probable errors. When the four constants are calculated from the experimental data for the range 920—1130°, the theoretical curve for the range 1130—1340° falls below the experimental curve to an extent which increases as the temperature rises. On the other hand, if the vapour pressures of lead are compared with those of mercury by making use of the modified isobaric temperature formula of Ramsay-Young, according to which T_1 and T_2 are connected by the formula

$$T_1/T_2 = m + nT_2 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

a very close agreement is observed. In spite of the wide difference between the boiling points, this formula permits of the calculation of isobaric temperatures [29] with an accuracy which lies within the limits of experimental error. Henglein's isobaric temperature formula does not give such good results, although the difference between the observed and calculated values is less than in the case of the Nernst formula. The boiling points of lead ($p = 760$ mm.) derived by extrapolation from the Ramsay-Young, the Henglein, and the Nernst formulæ are respectively 1619°, 1637°, and 1653°.

According to C. von Rechenberg,[30] it is quite a common occurrence for the vapour pressure curves of different liquids to intersect when the volatilities are of the same order. Such intersection is said to have been established for about two thousand pairs of liquids. It is apparent, however, that with very few exceptions, the intersecting curves are not experimental curves, but have been extrapolated by the application of Dühring's empirical formula on the basis of very meagre experimental data. In these circumstances, it seems quite possible that for a large proportion of the liquid pairs in question, the apparent intersection is a direct consequence of the method adopted in the extrapolation process.

[28] C. K. Ingold, *T.*, 1922, **121**, 2419.

[29] The data for mercury are those recorded by A. Smith and A. C. Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1447.

[30] *Z. physikal. Chem.*, 1921, **99**, 87; *A.*, ii, 120.

For a certain limited number of liquids there is, however, direct experimental proof of the intersection of the respective vapour pressure curves. To pairs of such liquids, the isobaric temperature formulæ of Ramsay-Young and of Henglein would not seem to be applicable. These formulæ take no account of the variation of the heat of vaporisation with the temperature and they can only be expected to apply to pairs of liquids for which the ratio of the heats of vaporisation is independent of the temperature. When one or both of such liquids are polymerised and the degree of polymerisation is a function of the temperature, it may be expected that formulæ of the Kirchhoff-Hertz or Nernst type will more accurately represent the experimental data.

The molecular heats of vaporisation calculated from $\lambda = 4 \cdot 23 S$,[31] where S is the slope of the approximately straight line curve obtained by plotting $\log p$ against $1/T$, are said to be in better agreement with the experimental values than are the latent heats calculated from the equations of Trouton, Bingham, or Nernst.

The boiling points of liquids which have been exposed to the action of phosphoric oxide for a number of years have been found [32] to be considerably higher than the normal values. The phenomenon is exhibited by liquids of different types, the observed increments ranging from 14° for hexane to 62° for mercury. In support of the view that the change in boiling point is due to polymerisation, preliminary measurements of the temperature coefficient of the surface energy indicate a considerable increment in the association factor. On the other hand, it is rather singular that no measurable differences are shown by the densities of the dried and undried liquids. The non-existence of such differences would seem to emphasise the tentative nature of the polymerisation hypothesis.

Crystallisation of Liquids.

A statistical investigation [33] of the probability of spontaneous crystallisation in supercooled liquids has led to the conclusion that crystallisation is provoked by colloidal dust particles, the effectiveness of which depends on their radius. Immediate crystallisation occurs if the radius of the dust particle is equal to that of a particle of the solid, which, according to thermodynamic considerations, would be in equilibrium with the supercooled liquid. If the dust particles have a smaller radius, the

[31] F. S. Mortimer, *J. Amer. Chem. Soc.*, 1922, **44**, 1429; *A.*, ii, 615.

[32] H. B. Baker, *T.*, 1922, **121**, 568; compare also H. B. Baker and Muriel Baker, *ibid.*, 1912, **101**, 2339.

[33] C. N. Hinshelwood and H. Hartley, *Phil. Mag.*, 1922, [vi], **43**, 78; *A.*, ii, 200.

average life of the supercooled liquid depends on the magnitude of the difference between the actual and the equilibrium radii.

From a study [34] of the number and distribution of the nuclei which are formed when thin films of liquid are allowed to crystallise between glass plates, it has been found that there is a very pronounced tendency for the nuclei to form in the outer zone of the film, particularly at the edge of the cover-glass. It is suggested that this tendency is a surface tension effect.

Experiments [35] made to determine the influence of pressure on the spontaneous crystallisation of supercooled liquids show that pressures up to about a thousand kilograms per square centimetre have very little influence on the number of nuclei which are formed, if the comparison is made at temperatures which are equally removed from the freezing points. The form of the curve which shows the connexion between the number of nuclei and the temperature is not appreciably altered by the application of pressure.

At a fixed temperature, the velocity of crystallisation of supercooled liquids is only slightly affected by subjecting the liquids to high pressures.[36] Since the applied pressure raises the freezing point, it is inferred that the intrinsic effect of the pressure is a diminution in the crystallisation velocity.

There is already a fair amount of evidence favourable to the view that the capacity of substances to form liquid crystals is determined by the molecular configuration, such crystals being formed when the molecules contain a long chain of atoms, and have a definite axis of symmetry. If in benzidine derivatives, which exhibit this property in a marked degree, a CH_2 group is introduced between the two benzene nuclei, substances are obtained which no longer possess the capacity to form liquid crystals. Similar results are found when the CH_2 group is replaced by CO, CS, S, or O, but when the interpolated chain is lengthened by the introduction of $-CH_2-CH_2-$ the property reappears. The derivatives of diphenylpropane do not, however, form liquid crystals, but the property reappears again in the derivatives of diphenylbutane. This alternating character is supposed [37] to be connected with the departure of the molecular configuration from the linear chain disposition.

Crystal Structure and the Lattice Elements.

In a recent lecture [38] to the Chemical Society, Sir W. H. Bragg has discussed the relations between the symmetry of crystals and

[34] K. Schaum, *Z. anorg. Chem.*, 1921, **120**, 241; *A.*, ii, 264.

[35] M. Hasselblatt, *ibid.*, 1921, **119**, 353; *A.*, ii, 35.

[36] *Idem*, *ibid.*, 325; *A.*, ii, 35.

[37] D. Vorländer, *Z. angew Chem.*, 1922, **35**, 249; *A.*, ii, 554.

[38] *T.*, 1922, **121**, 2766.

the probable symmetry of the ·molecule. The number of molecules in the unit cell depends on the respective symmetry numbers. If N is the number of asymmetric molecules which are required to produce crystal symmetry, and n is the number of molecules in the unit cell, the relation between these numbers is given by $N = nN'$, where N' is the symmetry number of the molecule. Since the great majority of organic crystals are monoclinic prismatic, N is equal to four and there should be four molecules in the unit cell if the crystal molecule is devoid of symmetry. The unit cells of naphthalene and anthracene contain two molecules, whilst those of acenapathene, α- and β-naphthols, benzoic acid,[39] salicylic acid, resorcinol, and 1 : 2-dinitrobenzene contain four molecules. The numbers of molecules in the unit cell indicated by these considerations are very much smaller than those assigned to the unit by K. Becker and W. Jancke,[40] who have examined a large number of aliphatic and aromatic compounds. Amongst these are included a long series of aliphatic acids, the structure of which varies according to whether the acids contain an even or an odd number of carbon atoms. Acids with an odd number of carbon atoms have a tetragonal lattice with twenty-four or forty-eight molecules in the unit cell. The data for acids with an even number of carbon atoms suggest, on the other hand, either hexagonal symmetry and a unit cell containing seventy-two molecules, or a rhombohedral lattice structure with twenty-four molecules in the unit cell. The alternating structure which is thus indicated by the X-ray examination of the aliphatic acids affords some explanation of the duality which is exhibited by this homologous series in regard to the melting point and other properties.

In these experiments the various substances were examined in the form of compressed pastilles. On submitting these to high pressures, evidence was obtained of a reduction in the volume of the unit cell amounting to about 10 per cent., the changes in the linear dimensions differing considerably according to whether the a, b, or c dimensions are in question.

An interesting development [41] in the technique of X-ray analysis is afforded by the replacement of homogenous beams by a continuous spectrum of X-radiation. A particular feature of the method is that it permits the use of short-waved penetrating rays and thereby facilitates the investigation of crystals of high absorbing power. Furthermore, the measured distances between the

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[39] Sir W. H. Bragg, *Proc. Physical Soc.*, 1921, **34**, 33; *A.*, ii, 28.

[40] *Z. physikal. Chem.*, 1921, **99**, 242, 267; *A.*, ii, 128.

[41] G. L. Clark and W. Duane, *Proc. Nat. Acad. Sci.*, 1922, **8**, 90; *A.*, ii, 483.

planes of atoms are independent of the constants of any other crystal.

The fact that the intensity of reflected X-radiation falls off rapidly as the glancing angle is increased has been interpreted [42] as evidence that the scattering power is not a localised effect but is the result of reflections originating in centres distributed throughout the atomic volume. From the form of the scattering curves, attempts have been made to determine the distribution of the electrons round the atomic nuclei.

From the behaviour of lithium fluoride, P. Debye and P. Scherrer came to the conclusion [43] that the relative numbers of the electrons surrounding the nuclei of fluorine and lithium are in the ratio 10 : 2. This would suggest that the valency electron of lithium (atomic number 3) has been transferred to the fluorine atom (atomic number 9) and might be interpreted as evidence favourable to the view that the constituents of such polar compounds are ionic and that the mechanism involved in the combination of polar elements is of the type postulated in the Lewis-Langmuir theory. The above value of the electron ratio depends, however, on an extrapolation of the actually measured scatterings to zero glancing angle, and for this and other reasons it would seem necessary to accept the conclusion with some reserve.

More recent observations [44] on crystals of sodium chloride, in which an attempt has been made to determine the absolute values of the scattering power of the sodium and chlorine atoms, represent a definite advance in the attack on the problem of electron distribution. From the data for the scattering at a series of glancing angles, curves are drawn which show the electron density at gradually increasing distances from the atomic centres. Hypothetical models of various kinds may obviously be tested by reference to these curves, which would appear to be definitely inconsistent with certain configurations which have been suggested for the sodium and chlorine atoms. Such excluded models of sodium chloride are those in which the sodium and chlorine atoms are represented as having outer shells containing eight electrons. An electron distribution of this type is inadmissible, whether the electrons be supposed to revolve in circular orbits of the same radius or to revolve in orbits on the same sphere. The experiments do not, as yet, indicate whether the valency electron of

[42] Sir W. H. Bragg, *Phil. Trans.*, 1915, [*A*], **215**, 253; A. K. Compton, *Physical Rev.*, 1917, **9**.

[43] *Physikal. Z.*, 1918, **19**, 474; *A.*, 1919, ii, 20.

[44] W. L. Bragg, R. W. James, and C. K. Bosanquet, *Phil. Mag.*, 1922, [vi], **44**, 433; *A.*, ii, 703.

sodium has been transferred to the chlorine. The difficulty in reaching a decision on this point is at once evident, when consideration is given to the fact that the distance between the centres of sodium and chlorine atoms is 2·81 Å., whilst the electron distribution curve (based on the measurement of the scattering power) extends to 1·0 Å. from the centre of the sodium atom and to 1·8 Å. from the centre of the chlorine atom.

Ionisation of Electrolytes.

The reception accorded to the views of Ghosh on the nature of solutions of electrolytes by the authors of certain well-known text books would seem to imply that these views have acquired the status of a well-established theory. The critical discussion of the theory by J. R. Partington,[45] D. L. Chapman and H. J. George,[46] H. Kallman,[47] C. A. Kraus,[48] J. Kendall,[49] and S. Arrhenius [50] conveys an entirely different impression and it is obvious that the Ghosh hypothesis is in many ways far from satisfactory as a basis for the interpretation of the behaviour of electrolytes. In particular, the facts and arguments adduced by Kendall represent a very strong case against the theory. The fundamental postulates are claimed to be inconsistent with one another, and by reason of the fact that an incorrect value has been assigned to the electrical work which is necessary to separate and disperse the ions from the average positions which they are supposed to take up in the postulated space lattice, all the equations derived by Ghosh are erroneous. Contrary to the requirements of the Ghosh theory, electrolytes of the same type are not equally ionised at equivalent concentrations, and the variation of μ/μ_∞ with temperature cannot be explained in terms of the change in the dielectric constant of the solvent medium. In the case of electrolytes of the simplest type, the osmotic coefficients derived from freezing-point data agree better with the values given by $i = 1 + \alpha$ (Arrhenius) than with those given by the Ghosh formula, according to which $i = 2\left(1 - \frac{1}{3}\log\frac{1}{\alpha}\right)$. Furthermore, in solvents of low dielectric capacity, the proportion of free ions should increase very rapidly with the dilution; the observed rate of increase is much smaller than that predicted by the theory.

This brief summary is sufficient to give some idea of the failure

[45] *Trans. Faraday Soc.*, 1919, **15**, 98; *A.*, 1920, ii, 151.
[46] *Phil. Mag.*, 1921, [vi], **41**, 799; *A.*, ii, 371.
[47] *Z. physikal. Chem.*, 1921, **98**, 433; *A.*, ii, 125.
[48] *J. Amer. Chem. Soc.*, 1921, **43**, 2514; *A.*, ii, 256.
[49] *Ibid.*, 1922, **44**, 717; *A.*, ii, 419.
[50] *Z. physikal. Chem.*, 1922, **100**, 9; *A.*, ii, 345.

of the Ghosh theory. The whole of the postulates involved in the theory are not thereby invalidated. There is, indeed, a growing tendency to regard more favourably the view that the strongly polar compounds are completely ionised and that the ratio μ/μ_∞ has not the significance attached to it in the theory of Arrhenius.

The refractive powers of electrolytes considered in the light of the dispersion theory have led to the conclusion [51] that there are considerable differences between the refractivities of atoms and the corresponding ions. A comparison of the refractivities of weak and strong electrolytes in aqueous solution indicates that the molecules of such substances can exist in two forms, one of which contains uncharged atoms or groups, whilst in the other "polarised" form, the constituent atoms or groups carry electric charges. Free ions and the ions in polarised molecules have the same structure and the same optical properties, which differ from those of the corresponding atoms or groups in the non-polarised molecules.

An attempt has been made [52] to determine the degree of ionisation of fused salts by measuring the refractivities.

The ionisation of picric acid,[53] dissolved in acetone, conforms to the requirements of the dilution law, the ionisation constant being of the order 1×10^{-6}. In aqueous acetone containing 6·2 per cent. of water, the dilution law is no longer satisfied. When the dilution is increased from 32 to 1024 litres, the value of $\alpha^2/(1-\alpha)v$ decreases some 50 per cent., which is approximately the deviation observed when the picric acid is dissolved in pure water. Since the "constant" for the aqueous acetone solutions is only about one-hundredth of the "constant" given by pure aqueous solutions, it would appear that the anomalous behaviour of strong electrolytes cannot be attributed to the high value of the degree of ionisation.

Electrical Conductance.

The experimental study of the mechanism of electrical conduction in solid binary compounds has not, until recently, given very clearly defined results. The difficulties incidental to transport measurements in solid conductors have, however, been overcome by C. Tubandt, who by this means has obtained positive information relative to the nature of the conducting process. The silver halides, lead chloride, and lead fluoride are electrolytic conductors. In the case of the silver compounds, the current is

[51] J. A. Wasastjerna, Z. physikal. Chem., 1922, 101, 193; A., ii, 491

[52] G. Meyer and A. Heck, Z. Elektrochem., 1922, 28, 2; A., ii, 241; Z. physikal. Chem., 1922, 100, 316; A., ii, 329.

[53] S. M. Neale, Trans. Faraday Soc., 1922, 17, 505; A., ii, 420.

carried exclusively by the positive ions, whereas the carriers in the lead compounds are the negative ions.[54] Cuprous sulphide, in the form which is stable above 91°, and silver sulphide in the form stable above 180° behave exactly like the silver halides. The β-form of silver sulphide, stable below 180°, is, however, a mixed conductor,[55] about 80 per cent. of the conduction being electrolytic and the remaining 20 per cent. metallic. As in the case of the α-form, the electrolytic conduction is due entirely to the movement of the silver ions. The passage of a current through β-silver sulphide is consequently a process in which positive electricity is conveyed by charged atoms, whilst negative electricity is conveyed in the opposite direction in the form of free electrons. The mechanism is therefore the same as that suggested by Kraus for the conductance of solutions of the alkali metals in liquid ammonia. The conductivity of these solutions increases rapidly [56] with increasing concentration, such that in saturated solutions at the boiling point of liquid ammonia, the atomic conductance of the alkali metals is considerably greater than the atomic conductance of mercury.

Interesting results have also been obtained [57] in the investigation of the mode of conduction of the current through mixtures of silver sulphide and metallic silver.

In measuring conductivities of solutions, the telephone receiver can be conveniently replaced [58] by a galvanometer in combination with a thermionic valve. A new differential method [59] is said to have given good results.

Potential Differences.

Low-voltage standard cells are described [60]; the combination Cd amalgam|CdI$_2$|PbI$_2$|Pb amalgam gives a constant and readily reproducible $E.M.F. = 0.09838$ volt at 20°.

Measurements [61] of the electrode potential H$_2$|HCl + KCl are said to afford evidence of the hydration of the hydrogen-ions.

The study [62] of electrodes of the type illustrated by the two examples,

[54] C. Tubandt and S. Eggert, Z. anorg. Chem., 1920, 110, 196; A., 1920, ii, 279. C. Tubandt, ibid., 1921, 115, 105; A., 1921, ii, 426.

[55] C. Tubandt, S. Eggert, and G. Schibbe, ibid., 1921, 117, 1; A., 1921, ii, 480.

[56] C. A. Kraus and W. W. Lucasse, J. Amer. Chem. Soc., 1922, 43, 2529; A., ii, 252.

[57] C. Tubandt and S. Eggert, Z. anorg. Chem., 1921, 117, 48; A., 1921, ii, 480.

[58] M. Abribat, Bull. Soc. chim., 1922, [iv], 31, 241; A., ii, 344.

[59] L. Rolla and L. Mazza, Gazzetta, 1922, 52, i, 421; A., ii, 544.

[60] J. Oblata, Proc. Phys. Math. Soc. Japan, 1921, [vii], 3, 136; A., ii, 343.

[61] E. Schreiner, Z. anorg. Chem., 1922, 121, 321; A., ii, 468.

[62] G. Trümpler, Z. physikal. Chem., 1921, 99, 9; A., ii, 110.

Ag|AgBr|KBr solution saturated with bromine

and   Cu|CuS|Na₂S solution saturated with sulphur,

indicates that there is an essential difference between such electrodes according to whether the solid binary compound is an electrolytic conductor (AgBr) or a metallic conductor (CuS). The experimental data suggest a fundamental difference in the structure of the two classes of compounds and the conclusion is drawn that the lattice elements of the compounds of the former group are ions, whilst those of the compounds which show metallic conduction consist of uncharged atoms.

Velocity of Hydrolytic Reactions.

A considerable amount of attention has been directed to the further investigation of the hydrolysis of sucrose and the esters. Although these reactions can be satisfactorily represented in terms of the ordinary velocity coefficient when the concentrations of the hydrolyte and the catalysing acid are fixed, it is well known that variations in the concentrations of the reactants produce changes in the velocity coefficient which suggest that the active masses of the hydrolyte, water, and catalyst are not appropriately measured by the respective volume concentrations. In recent work, the attempt has been made to replace volume concentrations by the activities or thermodynamic concentrations, the value of which, as shown by G. N. Lewis and M. Randall,[63] may be determined in a consistent manner from vapour pressure or osmotic data, and in the case of ionic reactants from potential difference measurements. To what extent the thermodynamic concentrations may afford a measure of the active mass of chemical reactants is a matter which can only be decided by experiment, and at the present time there appears to be no adequate ground for the presumption that thermodynamic concentrations provide a clue to the apparent deviations from the law of mass action.

Some experiments [64] on the rate of inversion of sucrose are interpreted in favour of the view that the hydrogen-ion and the un-ionised acid are both catalytically active. Other measurements [65] are said to be in agreement with the equation $dx/dt = ka_w{}^6 . a_H . (c_s - x)$, in which a_w and a_H are the activities of the water and the hydrogen-ion. According to this equation, the reaction is of the sixth order in so far as the water is concerned.

[63] J. Amer. Chem. Soc., 1921, 43, 233; A., 1921, ii, 241; ibid., 1150; A., 1921, ii, 427.

[64] R. H. Clarke, ibid., 1759; A., ii, 135.

[65] G. Scatchard, ibid., 2387; A., i, 230.

Experiments with sucrose [66] and ethyl acetate [67] in which the concentration of the hydrolyte was kept constant and the concentration of the catalysing acid was varied between wide limits lead to the conclusion that the reaction velocity is not by any means accurately proportional to the activity of the hydrogen-ion. The inversion data obtained with hydrochloric acid and acetic acid would indeed suggest that the specific character of the acid cannot be ignored.

Other observations [68] on the velocity of inversion, in which the concentration of the sucrose was varied from 100 to 700 grams per litre, have been found to yield a constant velocity coefficient when the participation of the sucrose, water, and hydrogen-ion is supposed to be proportional to the activities. The derivation of this coefficient involves, however, a number of other assumptions, namely, that the sucrose is mainly present in the solution in the form of a tetrahydrate, that the rate of inversion is determined by the rate of combination of a hypothetical sucrose dihydrate with the hydrogen-ion, and that the activity of the latter is very largely influenced by the viscosity of the medium. In these circumstances, it is very difficult to say whether the measurements in question are to be regarded as favourable or otherwise to the view that the active masses of the reactants are to be expressed in terms of the thermodynamic concentrations.

Measurements [69] of the rate of hydrolysis of ethyl acetate in presence of strong acids and varying quantities of the corresponding salts are said to indicate that the velocity is proportional to the cube root of the activity of the hydrogen-ion.

The initial velocities with which methyl and ethyl acetate are hydrolysed have been measured [70] at higher temperatures in presence of regulator mixtures, for each of which the p_H value was electrometrically determined. The velocity of hydrolysis shows a minimum at a definite hydrogen-ion concentration, but the curve obtained by plotting the velocity as a function of p_H is by no means symmetrical about the minimum point. The curve rises more steeply on the alkaline side of the " critical " p_H value, and from this, it may be inferred that the assumptions made by Wijs [71] in his determination of the degree of ionisation of water, are

[66] H. A. Fales and J. C. Morrell, *J. Amer. Chem. Soc.*, 1922, **44**, 2071; *A.*, ii, 832.
[67] H. S. Harned and R. Pfanstiel, *ibid.*, 2193; *A.*, ii, 832.
[68] T. Moran and W. C. McC. Lewis, *T.*, 1922, **121**, 1613.
[69] G. Åkerlöf, *Z. physikal. Chem.*, 1921, **98**, 250; *A.*, ii, 134.
[70] K. G. Karlsson, *Z. anorg. Chem.*, 1921, **119**, 69; *A.*, ii, 40.
[71] Compare *A.*, 1893, ii, 364; 1894, ii, 82.

unjustified. The presence of neutral salts does not affect the p_H value, for which the initial velocity of hydrolysis is a minimum.

Measurements [72] of the velocity of saponification of esters by potassium hydroxide in mixtures of ethyl alcohol and water show that the velocity coefficient is not a continuous function of the composition of the solvent. When the coefficients, measured at 15°, are plotted against the composition, a graph is obtained which consists of a series of straight lines intersecting at points which correspond closely with alcohol–water mixtures in which the components are present in simple molecular ratios. This coincidence is regarded as an indication of the formation of stable alcohol–water complexes. For the most part, the results appear to be independent of the nature of the ester. Furthermore, at higher temperatures, the number of discontinuities observed is smaller, indicating that the less stable complexes have disappeared. The interpretation given to the experimental data is said to be supported by the evidence afforded by the curves representing the variation of the physical properties of alcohol–water mixtures with the composition. Such curves are, however, for the most part, continuous and their interpretation is a matter of great difficulty. The difference between these curves and the discontinuous velocity curves is striking, but it seems possible that it may be due to the much greater susceptibility of reaction velocity to slight changes in the character of the solvent medium. On the other hand, it is rather remarkable that other reactions which have been studied in aqueous alcoholic media show no evidence of the discontinuities disclosed by the ester hydrolysis curves.

Combustion of Gases.

Considerations based on measurements of the speed of the uniform movement of flame in complex mixtures, that is to say, mixtures which contain oxygen and two or more combustible gases, have suggested [73] a new basis for the interpretation of the partition of the oxygen between the several combustible gases when the supply of oxygen is insufficient for complete combustion.

Under identical conditions, the speeds of propagation of flame are the same for all limit mixtures, provided that these are of the same type, that is, upper or lower limit mixtures. If the limit mixture of air and a combustible gas, A, is mixed with the limit mixture of air and a second combustible gas, B, the speed of propagation of flame in the resultant complex mixture is the same

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[72] H. McCombie, H. A. Scarborough, and R. H. Settle, *T.*, 1921, **119**, 970; 1922, **121**, 243, 2308.

[73] W. Payman and R. V. Wheeler, *ibid.*, 1922, **121**, 363.

as the speed characterising the simpler limit mixtures, and this equality holds no matter what may be the proportion in which the simple limit mixtures are present in the complex mixtures.

Other observations lead to the conclusion that this "law of speeds" is not a particular relation applicable only to limit mixtures, but that it holds for all complex mixtures, provided that the corresponding simple mixtures are of the same type.

So far as the propagation of flame is concerned, it follows that the air in the complex mixture, A + B + air, may be considered to be divided between A and B in such a way that the speeds of propagation of flame in the hypothetical simple mixtures, A + air and B + air, would be the same as it actually is in the complex mixture.

The products resulting from the passage of flame through a mixture of methane, hydrogen, and oxygen, in which the oxygen present is insufficient for the complete combustion of both combustible gases, should therefore be the same as would be obtained if the methane were mixed with a certain proportion of the oxygen, and the hydrogen with the remainder, and the two simple mixtures were separately exploded. Observations indicate in fact that this identity is actually obtained when the oxygen is distributed between the methane and the hydrogen so as to produce simple inflammable mixtures which are characterised by the same velocity of propagation of flame.

It has been supposed,[74] although the view has by no means been generally accepted, that the relative quantities of the two sets of products formed in the explosion of mixtures of two combustible gases with insufficient oxygen, afford a measure of the "relative affinities" of the two gases for oxygen. The considerations advanced by Payman and Wheeler indicate that the relative quantities of the products cannot be regarded as an effect of "affinity," but are a direct consequence of the fact that a methane–oxygen mixture, which has the same speed of flame as a given hydrogen–oxygen mixture, contains a considerably larger proportion of oxygen.

Further evidence [75] has been obtained in support of Le Chatelier's rule that when two or more limit mixtures containing different combustible gases are mixed, the resulting complex mixture is also a limit mixture. It appears, however, that there are exceptions to the rule and considerable deviations are found [76] when one of the combustible gases concerned is capable of propagating a cool flame. The propagation of this appears to be hampered

[74] W. A. Bone, *Phil. Trans.*, 1915, [*A*], **215**, 275.

[75] R. G. Boussu, *Compt. rend.*, 1922, **175**, 30; *A.*, ii, 557.

[76] A. G. White, *T.*, 1922, **121**, 2561.

by the presence of the second combustible gas, the resulting disturbance varying considerably with the nature of the latter.

The Radiation Theory of Chemical Change.

According to the simple form of the radiation theory,[77] the frequency of the radiation which transforms the molecules of a substance into a reactive condition can be calculated from the temperature coefficient of the velocity of the reaction. It is assumed that each molecule absorbs one quantum of the radiant energy in question. One of the objections raised against this view of the reaction mechanism is that the reacting substance shows no absorption band in the region of the calculated wavelength. The supporters of the theory contend, however, that such apparently simple, reactions may involve a series of consecutive changes, which, although they cannot be differentiated by any known experimental method, are sharply separated and clearly defined in terms of the associated energy quanta. In such a reaction, the energy absorbed per molecule will be represented as the sum of a number of smaller quanta which may, according to certain lines of evidence, bear some simple relation to one another.[78] In these circumstances, the bands in the absorption spectrum of the reacting substance will correspond with wave-lengths greater than that which is indicated by the simple radiation hypothesis. Infra-red bands corresponding with simple multiples of the calculated wave-length have in fact been found in the spectrum of nitrogen pentoxide, although no absorption occurs in the spectral region indicated by the simple theory. The radiation theory has also been criticised on the ground that the rate of supply of energy of the requisite frequency is totally inadequate to account for the observed rate of the chemical change. The validity of the argument is questionable. In any case, J. Perrin [79] points out that if the energy of activation corresponds with the absorption of a number of relatively small quanta, the requisite amount of energy is available in quantities more than sufficient to account for the observed velocity. On the other hand, W. C. McC. Lewis [80] contends that this objection falls to the ground, because it ignores the redistribution of the radiant energy which immediately ensues when radiation of a particular wave-length is removed.

A third criticism to which the radiation theory has been sub-

[77] Papers contributed to a general discussion arranged by the Faraday Society give a clear indication of the present position of the radiation theory; see *Trans. Faraday Soc.*, 1922, **17**, Part I; *A.*, ii, 628.

[78] E. C. C. Baly, *loc. cit.*, p. 588.

[79] *Loc. cit.*, p. 546.

[80] *Loc. cit.*, p. 573.

jected is that the reaction velocities are apparently unaffected by the directed radiation from external sources, although in such circumstances the density of the supposedly active radiation is enormously increased. This objection is also countered by the supposition that the energy of activation is the sum of a series of smaller quanta, and there would seem to be no necessity for Lewis's view that the effect of the active radiation is nullified by absorption in the solvent medium. The fact that the rate of inversion of sucrose by hydrochloric acid is not measurably altered [81] when the solution, in the form of a cloud of fine droplets, is subjected to the action of a beam of bright sunlight would seem to show that the latter view is untenable.

Summarising the position, it would appear that the radiation hypothesis cannot be reconciled with the facts so long as the energy of activation, E, is represented by the equation $E = Nh\nu$, where N is the Avogadro number, h the Planck quantum constant, and ν the frequency of the activating radiation. The simplicity of the relations involved in this equation constitutes probably the most attractive feature of the radiation hypothesis and if, as would seem to be the case, it is necessary to replace the above equation by one of the form $E = Nh(n_1\nu_1 + n_2\nu_2 + n_3\nu_3 \ldots)$, in which n_1, n_2, n_3 . . . are small integral numbers, then we have to deal with a modified radiation theory which, generally speaking, is no longer amenable to the test of experiment until such time as infra-red absorption spectra have been studied in a very thorough and comprehensive way.

There is always the possibility that in certain cases the general equation may be reduced to its simplest form. An example is said to be furnished by the decomposition of triethylsulphonium bromide,[82] the absorption spectrum of which has been examined in a number of solvents, in which the rate of decomposition had been previously measured at different temperatures by von Halban.[83] In the six solvents, where the reaction follows a normal course, maximum absorption is found to occur at a radiation frequency which agrees closely with that calculated from the temperature coefficient of the reaction velocity.

The two important facts which may be considered mainly responsible for the attention which has been given to the radiation hypothesis are that the hypothesis affords a plausible explanation of the effect of temperature on reaction velocity and provides a

[81] T. W. J. Taylor, *Nature*, 1921, **108**, 210; *A.*, ii, 336; compare also W. C. McC. Lewis, *ibid.*, 241; *A.*, ii, 336.

[82] W. C. McC. Lewis, *T.*, 1922, **121**, 665.

[83] *Z. physikal. Chem.*, 1909, **67**, 129.

basis for the interpretation of the mechanism of unimolecular reactions. It has, however, been pointed out,[84] that if the energy of activation corresponds with an additive series of quanta, the observed dependence of reaction velocity on the temperature is not that which would be indicated by the radiation theory. On the other hand, it may be doubted [85] whether there is any known instance of a chemical change in which the molecules of a substance are transformed independently of one another and of foreign molecules. A critical examination of the facts suggests rather that in all such chemical changes there is interaction between two or more molecules. Radioactive disintegration processes are not exceptional, for in such changes the chemical valency electrons are not involved, and, moreover, there is no temperature coefficient to be accounted for.

J. Plotnikow [86] criticises the law of photochemical equivalence on the ground that it is incompatible with the Grotthus-van't Hoff law, and that it leads to an impossible value for the chemical activity of radiant energy, the frequency of which is of the same order as that of Röntgen rays.

The thermal decomposition of formic acid [87] gives rise to two sets of products, namely, (a) carbon dioxide and hydrogen, (b) carbon monoxide and water. At 283°, the two reactions take place with the same velocity. From a consideration of the respective energies of activation it would appear that the formic acid should be exclusively decomposed into carbon monoxide and water. If the facts are to be interpreted in accordance with the simple radiation theory, it is necessary to introduce qualifying assumptions and the suggestion is made that the second reaction occurs on the walls of the containing vessel and that its velocity is enormously reduced by the surface conditions.

According to Perrin, fluorescence consists in the emission of characteristic radiation by the molecules of certain substances which are decomposed by light. This view is not in agreement with experiments which have been made by R. W. Wood.[88] For instance, it has been found that an aqueous solution of rhodamine is almost non-fluorescent at 100°, although at this temperature it is decomposed by light as rapidly as it is at the ordinary temperature. Perrin's theory further takes no account of the part played by oxygen in the photochemical decomposition of fluores-

[84] F. A. Lindemann, *Trans. Faraday Soc.*, 1922, **17**, 598.

[85] See, for instance, T. M. Lowry, *ibid.*, p. 596.

[86] *Z. wiss. Photochem.*, 1922, **21**, 134; *A.*, ii, 248.

[87] C. N. Hinshelwood, H. Hartley, and B. Topley, *Proc. Roy. Soc.*, 1922, [*A*], **100**, 575; *A.*, ii, 274.

[88] *Phil. Mag.*, 1922, [vi], **43**, 757; *A.*, ii, 334.

cent substances. The intensity of the fluorescence exhibited by a hydrochloric acid solution of fluorescein is independent [89] of the amount of oxygen present, although the rate of decomposition varies over a considerable range inversely as the oxygen content of the solution. In oxygen-free solutions, fluorescein is moreover stable towards light.

An interesting contribution [90] has been made to the photochemistry of silver compounds. It is shown that silver chloride is itself non-sensitive to light, and that the active absorbent of the light energy is the colloidal metallic silver which is present in very small amounts in fresh unilluminated silver chloride emulsions.

Disperse Systems and Colloidal Solutions.

Elutriation experiments,[91] made with powdered barytes and quartz, show that the rate of fall of small particles through water is not in agreement with the " law of viscous resistance," which states that the velocity varies as the square of the diameter. On the contrary, the connexion between the diameter, d, and the velocity, v, for particles of a given substance falling through water at a fixed temperature is given by the formula $\log d = \log a + kv$, in which a and k are constants. Under identical conditions, the sectional areas of the barytes and quartz particles which fall with the same velocity are in the same ratio as the gravitational forces which act on the two kinds of particles.

When Stokes's law is applied to the determination of the radius of the particles immersed in a liquid, no account is usually taken of the effect produced by adsorption. If r_0 denote the radius calculated in this way, r the true radius, and a the quantity of liquid adsorbed by one gram of the solid, then the relation [92] between these quantities is given by $r^2 = r_0^2\left(1 + a\dfrac{v_l}{v_s}\right)$, where v_l and v_s are the specific volumes of the liquid and solid respectively. On the assumption that the obvious external surface is responsible for the adsorption, this equation may be employed to determine an upper limit for the thickness of the adsorption layer.

The law of distribution of colloidal particles which represents the experimental data obtained by Perrin for suspensions of gamboge in water would appear to be limited in its application to a very narrow region below the surface of the suspensoid system. Observ-

[89] F. Weigert, *Z. Physik*, 1922, **10**, 349; *A.*, ii, 681.

[90] F. Weigert and W. Schöller, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 641; *A.*, ii, 10.

[91] T. M. Lowry and L. P. McHatton, *Trans. Faraday Soc.*, 1922, **18**, 19.

[92] A. M. Williams, *ibid.*, p. 53.

ations [93] on colloidal solutions of copper have shown that the particles are uniformly distributed, samples taken from a column, 90 cm. in height, which had been left undisturbed for fifty days, showing no measurable difference in concentration.

A further investigation [94] of gamboge suspensions, in which the counting of the particles at different depths was effected by a modified arrangement of the Zeiss ultra-microscope, shows that there are apparently three well-defined regions in a suspensoid system in addition to the surface layer, the thickness of which is only of the order of the range of intermolecular forces. The first of the three is the Perrin region, less than 0·1 mm. in thickness, in which the distribution of the particles is analogous to the distribution of the molecules in a column of gas; the second is a region, the thickness of which appears to be of the order of 1 mm., in which the departure from the logarithmic distribution formula becomes more and more pronounced as the distance from the surface increases; the third region is represented by the bulk of the suspension in which the distribution of the particles is sensibly uniform. The actual average results of the counts made in these experiments are shown in the accompanying table, in which y denotes the depth of the layer examined below the surface and n represents the number of particles per unit of volume :

y (cm.)	0·023	0·033	0·043	0·063	0·083	0·103	0·123	0·143
$n \times 10^6$	0·95	2·14	3·61	7·14	8·69	9·53	9·76	9·76

These numbers refer for the most part to the layer between the Perrin layer and the bulk of the suspension. Theoretical considerations put forward independently by Burton and by Porter lead to equations which are in agreement with the observed distribution in this transition layer.

If a measured volume of the saturated solution of a lead salt containing one of its radioactive isotopes is shaken up with a weighed quantity of the finely-powdered solid (free from the isotope), it may be assumed that the isotope will distribute itself between the surface of the solid and the solution in the same ratio as the lead. By measuring the change in the radioactivity of the solution, it is possible to estimate [95] the surface area of the finely divided solid lead salt. A convenient summary of other applications of radioactive substances in the investigation of molecular dynamics is given in a paper under the title " Radioactive Indicators." [96]

[93] E. F. Burton and (Miss) E. Bishop, *Proc. Roy. Soc.*, 1921, [*A*], **100**, 414.

[94] A. W. Porter, *Trans. Faraday Soc.*, 1922, **18**, 91.

[95] F. Paneth and W. Vorwerk, *Z. physikal. Chem.*, 1922, **101**, 445; *A.*, ii, 618.

[96] F. Paneth, *Z. angew. Chem.*, 1922, **35**, 549; *A.*, ii, 785.

Facts are adduced [97] in support of the view that, in certain cases at least, the adsorption of radioactive substances from solution is not primarily determined by the colloidal condition of the adsorbent but by its chemical nature.

Liquids which have been adsorbed by porous substances appear to be subjected to a very high degree of compression as a result of the action of molecular forces.[98] The change in the volume of water adsorbed in the micro-pores of charcoal is probably of the order of 25 per cent. and in the case of ether about 40 per cent.

The conditions determining the formation of amorphous or crystalline solids in precipitation changes are discussed by F. Haber.[99] It is to be expected that the rate at which the primary non-orientated aggregates will be transformed into ordered lattice formations will be greatest in the case of binary compounds, in which the polarity is most marked. When the polarity is less strongly accentuated, the compounds will tend to remain in the primary form of amorphous precipitate or sol.

Zeolites, when partly or completely dehydrated, absorb gases in large quantities.[1] In general, the volumes of the different gases which are taken up, increase in the order of the respective critical temperatures. Hydrogen is, however, absorbed in exceptionally large quantities, and the behaviour of hydrogen and certain other gases suggests that these enter into the crystal lattice in the position previously occupied by the water of hydration.

The connexion between the coagulating power of ions and the concentration of the disperse phase is found [2] to depend on the nature of the latter. For colloidal solutions of chromic oxide, Prussian blue, and ferric oxide, the coagulating ion-concentration decreases as the concentration of the colloid decreases, irrespective of the valency of the ion. On the other hand, when the disperse-phase is arsenious sulphide, the relation between the concentrations of the ion and of the colloid varies very considerably according to the valency of the ion. The differences in behaviour are attributed to the relative adsorbabilities of the coagulating positive ion and of the stabilising negative ion.

The action of protective colloids [3] in retarding changes of state is shown very clearly in the precipitation of mercuric iodide in

[97] E. Ebler and A. J. van Rhyn, *Ber.*, 1921, **54**, [B], 2896; *A.*, ii, 16.

[98] W. D. Harkins and D. T. Ewing, *J. Amer. Chem. Soc.*, 1921, **43**, 1787; *A.*, ii, 123.

[99] *Ber.*, 1922, **55**, [B], 1717; *A.*, ii, 553.

[1] R. Seiliger and K. Lapkamp, *Physikal. Z.*, 1921, **22**, 563; *A.*, ii, 30.

[2] H. B. Weiser and H. O. Nicholas, *J. Physical Chem.*, 1921, **25**, 742; *A.*, ii, 266; E. F. Burton and E. D. MacInnes, *ibid.*, 517; *A.*, ii, 130.

[3] J. N. Friend, *Nature*, 1922, **109**, 341; *A.*, ii, 267.

presence of one per cent. of gelatin. The initially precipitated yellow modification remains unchanged for a considerable time.

The conclusions which have been drawn from the study of soap solutions by the application of various osmotic methods and by measurements of conductivity, potential differences, and catalytic activity have been confirmed in a remarkable way [4] by the behaviour of the solutions when they are subjected to ultra-filtration. Not only has an independent check on the results of previous work been thereby obtained, but it is shown that ultra-filtration affords a method for the separation of the ionic micelle from the neutral colloid, for the determination of the degree of hydration of the colloidal constituents, and for the approximate determination of the dimensions of the charged and uncharged colloidal particles. The ionic micelle is mainly composed of aggregated ions with water of hydration, whilst most of the neutral colloid is present in quite separate particles of much larger dimensions.

The theory of ultra-filtration is discussed and on the assumption that pores of a given diameter will allow particles of a smaller diameter to pass through provided that the applied pressure is greater than the osmotic pressure of the constituents which are coarse enough to be held back by the pores, it is found that the experimental results can be adequately explained.

The ultra-filtration method has already been applied in the investigation of other colloid-electrolyte systems. The successful application of the method would seem to depend on the rapidity with which any disturbance of the internal equilibrium is annulled in comparison with the speed of the ultra-filtration process.

The properties of hexadecanesulphonic acid [5] indicate that this acid is a typical colloidal electrolyte having all the characteristic properties of the alkali-metal soaps. Ring compounds are far less colloidal than the corresponding open-chain compounds, indicating that the linear extension of the molecule is an important factor in producing a colloidal electrolyte.

Soap solutions, to which the corresponding alkali metal chloride has been added in quantities insufficient to cause salting out, are found [6] to contain the soap for the most part in the form of neutral colloid, the proportion of ionic micelle being much smaller than in pure soap solutions.

The consideration of the salting-out process from the point of view of phase equilibrium leads to the conclusion [7] that a colloidal

[4] J. W. McBain and W. J. Jenkins, *T.*, 1922, **121**, 2325.

[5] (Miss) M. H. Norris, *ibid.*, 2161.

[6] C. S. Salmon, *ibid.*, 711.

[7] J. W. McBain and A. J. Burnett, *ibid.*, 1320.

solution, in which true reversible equilibria subsist, behaves as a single phase towards other phases with which it is in equilibrium.

On the other hand, for equilibria within the colloidal solution, it seems to behave as a multiphase system having one more degree of freedom than that which would be assigned to it by the ordinary phase rule.

H. M. DAWSON.

INORGANIC CHEMISTRY.

THE study of radioactivity, isotopy, and atomic constitution has assumed such importance that a separate Report is now devoted to these developments of inorganic chemistry, and atomic constitution is here discussed solely from the stand-point of valency and the ordinary chemistry of the elements. Nevertheless, the bulk of orthodox inorganic chemical work, including as such those cases in which the application of physical methods is of interest for the results attained rather than for the methods employed, is so great that the Report can only be kept within the prescribed limits by ruthless economy of words and omission of much interesting material. An effort has been made, however, to report precisely, rather than to comment on, as much as possible of the work deemed to be of general interest to chemists.

Atomic Theory.

Langmuir has deduced the types of valency, and its numerical values, for most elements by a method simpler than that formerly employed,[1] and, on the basis of the electron theory of chemistry, Sir J. J. Thomson[2] has attributed structures to the unit cells of elements according to their valency, and has calculated therefrom values for bulk-modulus, critical frequency, and dielectric constant which agree with experimental values. It has been found[3] that carbon dioxide and nitrous oxide have identical viscosities over the range 0—100°, and it is inferred that their molecular dimensions are the same, in agreement with Langmuir's view that both molecules have the same arrangement of the outer electrons.

The principle of induced alternate polarity of atoms, previously applied to explain many properties of organic compounds, has now been derived simultaneously and independently by Lapworth[4] and by Kermack and Robinson,[5] as a necessary consequence of the electron theory. It is perhaps important to observe that in both

[1] I. Langmuir, *Science*, 1921, **54**, 59; *A.*, ii, 137.

[2] Sir J. J. Thomson, *Phil. Mag.*, 1922, [vi], **43**, 721; *A.*, ii, 355.

[3] C. J. Smith, *Proc. Physical Soc.*, 1922, **34**, 155; *A.*, ii, 549.

[4] A. Lapworth, *T.*, 1922, **121**, 416.

[5] W. O. Kermack and R. Robinson, *ibid.*, 427.

cases it is found desirable to postulate union of atoms, not only by the normal " single " or " double " bond, consisting in the sharing by adjacent atoms of two or four electrons, respectively, but also by the sharing of one or three electrons. A bond of three electrons has already been proposed as affording the most rational expression of the constitution of benzene, and a single electron bond has been supposed probable,[6] so that there is no special difficulty in accepting the variation of the Lewis–Langmuir hypothesis. Thus among the elements of the First Period this theory continues to prove adequate.

Difficulties begin with sodium and increase among the heavier elements, where it becomes evident that the usual hypothesis is at best no more than a first approximation to the truth about atomic constitution, accounting well enough for the broad similarities within and differences between the various groups, but failing to give, for example, as any hypothesis pretending to finality must give, a theoretical basis for the detailed differences observed within each group. Reviewing such differences, one cannot escape the conclusion that chemical properties are determined, not by the outer electrons alone, but by the atomic constitution as a whole; and if this is so, the assumption, now general, that the chemical properties of isotopes are identical, whilst probably true or very nearly true for the heavier elements, may not hold for the lighter elements. It is thus important to consider the several attempts which have been made to amend the original hypothesis.

From a consideration of emission spectra, Bohr has developed a dynamic theory of the structure of the heavier elements, postulating eccentric orbits for certain electrons (which thus belong, in a sense, to more than one level in the atom), and irreconcilable with any conception of sharply separated shells of electrons,[7] which accounts for the colour (in compounds), paramagnetism, and relative complexity of spectra of the elements and is strongly supported by recent work upon the X-ray spectra.[8] Measurements of the intensity of reflection of X-rays per unit volume of the units constituting crystalline sodium chloride[9] may be interpreted as showing the existence in successive shells, counting outwardly, of 7 and 3 electrons in the sodium atom, and of 10, 5, and 3 electrons in the chlorine atom; or, alternatively, give for the variation of electron density with distance from the centre of each atom values which agree well with those calculated for an atom of the type proposed by

[6] Sir J. J. Thomson, *Phil. Mag.*, 1921, [vi], **41**, 538; *A.*, ii, 279.

[7] N. Bohr, *Z. Physik*, 1922, **9**, 1; *Nature*, 1921, **108**, 208; *A.*, ii, 363, 277.

[8] D. Coster, *Phil. Mag.*, 1922, [vi], **43**, 1070; **44**, 546; *A.*, ii, 491, 677.

[9] W. L. Bragg, R. W. James, and C. H. Bosanquet, *ibid.*, 1922, **44**, 433; *A.*, ii, 703.

Bohr; but appear to show clearly that there is not in either atom of sodium chloride a shell of eight electrons.

From the chemical point of view come attempts to bring the static hypothesis into closer accord with the facts by modifying Langmuir's fourth postulate. Bury's modification [10] reads : "The maximum number of electrons in each shell or layer is proportional to the area of its surface; thus successive layers can contain 2, 8, 18, and 32 electrons. Groups of 8 and 18 electrons in a layer are stable, even when that layer can contain a larger number of electrons. The maximum number of electrons in the outer layer of an atom is 8 : more than 8 electrons can exist in a shell only when there is an accumulation of electrons in an outer layer. During the change of an inner layer from a stable group of 8 to one of 18 or from 18 to 32, there occurs a transition series of elements which can have more than one structure." This leaves unchanged the structures assigned by Langmuir to the elements of the First Period, but gives to all succeeding elements new structures which are in better accord with Bragg's atomic diameters and satisfactorily explain many chemical properties, for example, the similarities and differences in the triplets of Group VIII and the existence and characters of the rare earths. It seems significant, too, that Bury's structures for the inert gases are similar to those deduced by Bohr from the emission spectra. The argument of the paper cannot be reproduced in abstract and those interested will find that the original paper repays careful study. It has since been shown [11] that Bury's structures afford probabilities of complexity of spectra in general agreement with the observed numbers of lines for many elements.

Another alternative disposition of electrons (2 : 8 : 18 : 32 : 18 : 8 instead of Langmuir's 2 : 8 : 8 : 18 : 18 : 32) has been suggested by Dauvillier,[12] as a result of investigations of the L- and K-series lines in the X-ray spectra of a number of the heavier metals; and he too supposes that chemical properties are in part dependent on the internal electrons, and that inner electron shells may be incomplete. Regarding the "atomic radius" as the distance from the centre to an electron group in the valency shell, it has been shown that the distance between atomic centres is often less than the sum of the atomic radii : a number of causes may be adduced to explain the fact, among which the conception of bonds of more than one electron and the possibility of more than one arrangement of electrons within the atomic sphere [13] are of interest, as they have already been

[10] C. R. Bury, *J. Amer. Chem. Soc.*, 1921, **43**, 1602; *A.*, ii, 43.

[11] H. S. King, *ibid.*, 1922, **44**, 323; *A.*, ii, 277.

[12] A. Dauvillier, *J. Phys. Radium*, 1922, [vi], **3**, 154, 221; *Compt. rend.*, 1921, **173**, 1077; *A.*, ii, 559, 678, 43.

[13] M. L. Huggins, *Physical Rev.*, 1922, **19**, 346; *A.*, ii, 634.

supposed, on quite other grounds, to be possible. The suggestion is made that, in the second and third shells, the fifth and subsequent electrons pair with the first four to give a tetrahedral arrangement of pairs, and that the forces causing pairing result, in the case of the heavier elements, in the formation of triplets of electrons in the inner shells.[14]

This stimulating clash of theories evidently arises in part because chemical phenomena can best be interpreted by a static conception of the atom whilst physical evidence demands a dynamic conception. Therefore special interest attaches to the suggestion made by Sir Oliver Lodge [15] that these views might be reconciled were chemical union attributed, not to electrical attraction between the atoms, but to interlacing of the stationary magnetic fields which must accompany rapidly revolving electrons. Theories of magnetism clearly tend to assume a form favourable to such an hypothesis; [16] and to the connexion between chemical constitution and magnetic properties in compounds, developed chiefly by Pascal (whose recent work confirms the usual view of the constitution of the acids of sulphur, phosphorus, and arsenic),[17] is given new significance by experiments showing that ferro-magnetism is increased in iron and actually imparted to manganese by fusion in hydrogen, whilst the magnetic susceptibility of palladium is reduced by the adsorption of hydrogen. These phenomena may be explained by the assumption that the entry of hydrogen into the electron system of the metal produces a new system corresponding with the element of next higher atomic number, in the case of manganese, iron; in that of palladium, silver.[18]

Atomic Weights.

Glucinum.—Basic glucinum acetate, prepared from the technical carbonate, was recrystallised from glacial acetic acid until free from iron, sublimed, and converted into nitrate, which was dissolved in ammonium carbonate. Glucinum carbonate precipitated from this solution was calcined to oxide, and this, by ignition with carbon in a current of chlorine, gave the pure chloride, which was collected and weighed with exclusion of water. The ratios $GlCl_2 : 2Ag$ and

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[14] M. L. Huggins, *Science*, 1922, **55**, 459; *J. Amer. Chem. Soc.*, 1922, **44**, 1841; *A.*, ii, 632, 744.

[15] Sir O. Lodge, *Nature*, 1922, **110**, 341; see also W. Hughes, *ibid.*, 1922, **110**, 37; *A.*, ii, 701, 632.

[16] For a useful summary, see A. E. Oxley, *Nature*, 1923, **111**, 54.

[17] P. Pascal, *Compt. rend.*, 1921, **173**, 712; 1922, **174**, 457, 1698; *A.*, 1921, ii, 692; 1922, ii, 285, 564.

[18] A. E. Oxley, *Proc. Roy. Soc.*, 1922, [*A*], **101**, 264; *A.*, ii, 469.

GlCl$_3$: 2AgCl were determined in the usual manner, the mean result of all analyses being the value Gl = 9·018,[19] appreciably lower than the accepted value Gl = 9·1.

Boron.—By the methods used in the foregoing determination, the same authors [20] have measured the ratios BCl$_3$: 3Ag and BCl$_3$: 3AgCl, three samples of purified boron trichloride giving the mean values B = 10·840, 10·818, and 10·825, respectively. The first value is rejected for discordance and the rounded mean of the latter two values, B = 10·82, is taken.

Baxter and Scott [21] reduced boric oxide with excess of magnesium, extracted with hydrochloric or hydrobromic acid, and treated the resulting boron at 700° with chlorine or with argon saturated with bromine vapour. The samples of chloride or bromide thus prepared were freed from excess of halogen and repeatedly distilled through Hempel fractionating columns in evacuated glass apparatus. Each then gave, when compared with silver in the usual way, the value B = 10·83 ± 0·01. These results, differing by no more than 1 part in a thousand, are a great improvement on those formerly available, and accord much better with the isotope ratio determined by Aston than, for example, the value B = 10·900 found by Smith and van Haagen.[22]

Yttrium.—Yttria, prepared from Norwegian gadolinite and purified by a rigorous and prolonged process of fractional crystallisation (as bromate) and fractional precipitation, converted into chloride and titrated with weighed silver in the usual way gave, as the mean of twenty-one values varying from 88·97 to 89·08, the value Yt = 89·03.[23]

Lanthanum.—The low value, La = 138·91, found by Baxter, Tani, and Chapin,[24] has been confirmed by determination of the ratio LaCl$_3$: 3Ag using spectroscopically pure lanthanum chloride. Ten experiments gave for the atomic weight extreme values of 138·84 and 138·97, with a mean La = 138·89.[25] It seems clear, therefore, that the international figure, La = 139·0, is too high.

Some work has been recorded on measurement of atomic weights

[19] O. Hönigschmid and L. Birckenbach, *Ber.*, 1922, **55**, [B], 4; *A.*, ii, 214.

[20] *Anal. Fís. Quím.*, 1922, **20**, 167; *A.*, ii, 641.

[21] G. P. Baxter and A. F. Scott, *Science*, 1921, **54**, 524; *A.*, ii, 285.

[22] E. F. Smith and W. K. van Haagen, *Carnegie Inst. Pub.*, 1918, **267**, 1; *A.*, 1920, ii, 247.

[23] H. C. Fogg and C. James, *J. Amer. Chem. Soc.*, 1922, **44**, 307; *A.*, ii, 297.

[24] G. P. Baxter, M. Tani, and H. C. Chapin, *ibid.*, 1921, **43**, 1080; *A.*, 1921, ii, 454.

[25] B. S. Hopkins and F. H. Driggs, *ibid.*, 1922, **44**, 1927; *A.* ii, 770.

by physical methods. Forty-five determinations gave a mean value of 1.42897 ± 0.00007 grams for the weight of the litre of oxygen at $0°$ and 760 mm. in latitude $45°$, in close agreement with other recent work on this constant but less by 0.00008 gram than the accepted value.[26] Recalculation from the known density of hydrogen bromide, using the new value for oxygen, gives Br = 79.927.[27]

Determinations of the normal density and compressibility of carbon dioxide and ethylene [28] give values for the atomic weight of carbon, 11.998 and 12.000, respectively, appreciably lower than the international value, C = 12.05, but in better accord with atomic theory; and the gravimetric determinations of Richards and Hoover have been criticised.[29] On the other hand, a strong protest has been entered [30] against such use of atomic weights derived from gas densities in criticism of " chemical " atomic weights, and supported by proof [31] that the proportion of impurities in atomic weight silver and iodine is very much smaller than has been alleged.[32]

Chemical Reaction.

Before proceeding to deal with individual elements in Group order, consideration must be given to certain results which cannot be placed in any definite category (unless we invoke the hard-pressed word catalysis) and yet are clearly of fundamental significance.

Baker has extended the experiments previously reported.[33] Pure liquids were sealed up in Jena-glass flasks with pure phosphoric oxide and after lapse of time were opened to atmospheric pressure through dry mercury and gradually heated, precaution being taken to avoid superheating : the temperature of steady ebullition was taken as the boiling point with the results given in the table : [34]

[26] E. Moles, *J. Chim. physique*, 1921, **19**, 100; E. Moles and F. González, *Anal. Fís. Quím.*, 1922, **20**, 72; E. Moles and M. Crespi, *ibid.*, 190; *A.*, ii, 141, 497, 636.

[27] E. Moles, *J. Chim. physique*, 1921, **19**, 135; *A.*, ii, 140.

[28] Ph. A. Guye and T. Batuecas, *Helv. Chim. Acta*, 1922, **5**, 532; T. Batuecas, *ibid.*, 544; *A.*, ii, 617, 618.

[29] E. Moles, *Anal. Fís. Quím.*, 1921, **19**, 255; *A.*, ii, 51.

[30] G. P. Baxter, *J. Amer. Chem. Soc.*, 1922, **44**, 595; *A.*, ii, 370.

[31] G. P. Baxter and L. W. Parsons, *ibid.*, 577; G. P. Baxter, *ibid.*, 1922, **44**, 591; *A.*, ii, 376, 377.

[32] P. A. Guye and F. E. E. Germann, *Compt. rend.*, 1914, **159**, 225; *A.*, 1914, ii, 727.

[33] H. B. Baker and Muriel Baker, *T.*, 1912, **101**, 2339.

[34] H. B. Baker, *ibid.*, 1922, **121**, 568.

	Period of drying (years).	Original boiling point.	New boiling point.	Rise in boiling point.
Bromine	8	63°	118°	55°
Mercury	9	358	420—425	62
Hexane	8½	68·4	82	14
Benzene	8½	80	106	26
Carbon disulphide ...	1+27	49·5	80	30
,, tetrachloride...	9	78	112+	34
Ethyl ether	9	35	83	48
Methyl alcohol	9	66	120+	54
Ethyl alcohol	9	78·5	138	60
Propyl alcohol	9	95	134	39

These large differences of boiling point are undoubtedly real. The mercury maintained at 360° for thirty minutes did not boil and gave only a trace of condensate above the liquid: the hexane was transferred to another flask, not specially dried, and still boiled at 81°: water could be boiled through the benzene with only slow evaporation of the latter: and the ether at 20° had a vapour pressure of 374 mm. only, as against the normal value of 442 mm. The liquids recover their normal boiling points on exposure, even to air dried with sulphuric acid and phosphoric oxide; benzene slowly, ethyl ether and the three alcohols very rapidly.

Comparative experiments with dried and undried bromine, benzene, hexane, and nitrogen tetroxide showed that the capillary rise increased steadily during drying to a value which indicates an increase of molecular weight to 1·5—3·0 times that for the normal liquids. These results clearly support the earlier hypothesis that drying shifts the equilibrium between normal and associated molecules; possibly because absence of water hinders or inhibits dissociation, as it is known to do in the case of certain vapours, and has no effect or a smaller effect on the opposing association. If, as is usually supposed, the degree of association of a liquid is increased by lowering of temperature, information as to whether association is stopped or merely hindered might be obtained by ascertaining the ultimate effect of drying different specimens of the same liquid maintained at widely different temperatures throughout the whole period of drying. It has been shown, rather unexpectedly, that in benzene, carbon tetrachloride, carbon disulphide, ether, bromine, sulphur dioxide, and nitrogen trioxide, drying produces no change in volume as great as 1 part in 10,000.

Thermometers suspended in the vapour from dry hexane and benzene, boiling at 82° and 106°, respectively, showed temperatures of 68·4° and 80°, the boiling points of the normal liquids; a very curious result. Smits had previously suggested [35] that, supposing internal change to be inhibited by drying, fractional distillation

. [35] A. Smits, Z. physikal. Chem., 1922, **100**, 477; A., ii, 358.

should result in a separation of the normal and associated liquids, and later experiments [36] have shown that if a specimen of dried benzene is distilled over completely, the temperature of a thermometer suspended in the vapour shows a steady rise, indicating that fractional distillation does, in fact, occur.

Apparently, similar changes may take place in the solid state, preliminary experiments having shown that the melting points of sulphur and iodine, originally 112·5° and 114°, are, after nine years' drying, 117·5° and 116°, respectively.

It has been found [37] that the reactivity of ammonia, measured by the expansion at constant temperature resulting from its partial dissociation in contact with an activated platinum wire heated by a definite current for a definite time, is the same for ammonia obtained by slow escape from a commercial cylinder of liquid ammonia, by heating aqueous ammonia and drying the gas with quicklime, or by liquefying either preparation and allowing it to evaporate isothermally at its boiling point. Under the same conditions, ammonia allowed to escape very rapidly from a cylinder had a much lower reactivity, and it is concluded that an " inactive " phase of ammonia has thus been obtained which contains more molecules of the type characteristic of liquid ammonia [38] than are normally present in the " active " phase, and that the existence of such active and inactive phases explains the chemical inactivity of dried gases and supports the radiation theory of chemical reactivity.[39]

It may be suggested, however, that the experimental results will bear a simpler, if less significant, interpretation. It is known that ordinary commercial ammonia, dried over lime, contains about 1 per cent. of water,[40] and that rapid, irreversible distillation such as may occur by free discharge of gas from a cylinder of liquid is a very effective means of separating the constituents even of a constant-boiling mixture,[41] so that the gas thus obtained may well be considerably drier than that in real equilibrium with the cylinder liquid. Baly has found that addition of water vapour to ordinary ammonia increases its reactivity, drying certainly decreases its reactivity, and so the greater dryness of the " inactive " form would appear to be capable of explaining the whole of the observations, including the " recovery " of the gas in cylinders on standing (by

[36] H. B. Baker, private communication.
[37] E. C. C. Baly and H. M. Duncan, T., 1922, **121**, 1008.
[38] The " liquidogen " molecules of Traube, Ann. Physik, 1902, [iv], **8**,
[39] E. C. C. Baly, Phil. Mag., 1920, [vi], **40**, 15; Trans. Faraday Soc., 1922, **17**, 588; A., ii, 628.
[40] See, e.g., A. G. White, T., 1922, **121**, 1688.
[41] See, e.g., R. S. Mulliken, J. Amer. Chem. Soc., 1922, **44**, 2389; A., 1923, ii, 31.

acquisition of the equilibrium content of water vapour), identity of slowly released cylinder gas with laboratory preparations dried by lime, recovery of " inactive " gas in the experimental tube when the wire is heated at 200° (release of adsorbed water from the wire or walls), and the increase in reactivity of " inactive " ammonia with increase of temperature of the wire (the five pairs of figures given show that twenty seconds' heating with currents of 4·00, 4·10, 4·25, 4·35, and 4·50 amps. produces decomposition in the ratios active/inactive = 2·18, 1·76, 1·60, 1·46, and 1·35, respectively).

The " activation " of chlorine by light, a subject of much past controversy, has been reaffirmed. A rigid series of experiments [42] proves that when chlorine is exposed to sunlight or intense ultra-violet light and mixed with hydrogen in the dark, reaction occurs immediately on exposure of the mixture to the light of two 100-watt tungsten lamps, whilst with chlorine not so insolated reaction is delayed by the known " induction period " of about two minutes. The effect of insolation persists in the dark for three hours, but is diminished after twenty-four hours and disappears after several days. An equally rigorous series of experiments shows that chlorine exposed to the light of a 3000-watt Bovie quartz mercury lamp or to a high tension discharge will not react with hydrogen in the dark even when the interval between insolation and mixing is only 0·01 second, so that any explanation of activation in terms of the forma-tion of a triatomic or other active form of chlorine seems improbable.

A globule of fused calcium chloride between two copper wires shows great decrease in resistance in presence of a trace of moisture, and use of this device as a " detector " has shown [43] that pure hydrogen reacts with copper oxide at a definite and reproducible temperature, which is lowered some 20° if the hydrogen first passes over platinised asbestos. Similar results were obtained with hydro-gen and sulphur, formation of hydrogen sulphide (detected by lead acetate paper) occurring at a lower temperature if the hydrogen first passed over palladium black. The activated hydrogen was found to be ionised, but only to an extent considered altogether insufficient to explain reaction; and the persistence of the pheno-menon when glass wool was interposed between the platinised asbestos and copper oxide and the absence of any change in refractive index by activation or increase of volume on decay seem to show that the observed effects cannot be attributed to monatomic or triatomic hydrogen. The explanation advanced is that the internal

[42] G. L. Wendt, R. S. Landauer, and W. W. Ewing, *J. Amer. Chem. Soc.*, 1922, **44**, 2377; *A.*, 1923, ii, 22.

[43] P. Anderson, *T.*, 1922, **121**, 1153; see also, R. N. Pease and H. S. Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2179; *A.*, ii, 148.

energy of the hydrogen molecules is increased by contact with the platinum or palladium : this should result, presumably, in a lowering of the temperature of the metal, and the explanation might thus be tested experimentally.

Lastly, reference may be made to the mysterious variation observed [44] in the rate of decomposition of mercuric fulminate in a vacuum at 80°, which seems to bear some resemblance to the foregoing unexplained phenomena.

The Inert Gases.

A spectrophotometric method has been developed for the estimation of krypton and xenon in admixtures with argon.[45] Positive-ray analysis of the residues from a thousand tons of liquid air has given evidence of new constituents of the atmosphere with molecular weights 163 and 260; but the observed lines may be due to diatomic molecules of xenon and krypton.[46]

Precise determinations show that the solubility of helium has not, as was supposed, a minimum at 20°.[47] A detailed account of the distribution, sources, and chemical composition of helium-bearing natural gases has been published.[48]

Anderson has shown [49] that in the explosion of metallic wires by heavy condenser discharges a temperature of some 20,000° is attained in the wire in 1/300,000 second. It is now reported that thin tungsten wires exploded in this way yield gas which when obtained in a vacuum shows the helium spectrum, and if obtained in an atmosphere of pure carbon dioxide and measured after absorption of the latter in alkali has, as the mean of twenty-one experiments, a volume which corresponds to an amount of helium about 25 per cent. of the weight of tungsten taken.[50] This result, if confirmed, would appear to be the first case of atomic decomposition by artificial means.

Group I.

Active hydrogen [51] has been prepared in the Siemens ozoniser, using both induction coil discharge and a Tesla discharge of much higher frequency and voltage, and also by passing pure hydrogen

[44] R. C. Farmer, *T.*, 1922, **121**, 174.

[45] C. Moureu and A. Lepape, *Compt. rend.*, 1922, **174**, 908; *A.*, ii, 394.

[46] Sir J. J. Thomson, *Proc. Roy. Soc.*, 1922, [A], **101**, 290; *A.*, ii, 565.

[47] H. P. Cady, H. M. Elsey, and E. V. Berger, *J. Amer. Chem. Soc.*, 1922, **44**, 1456; *A.*, ii, 642.

[48] G. S. Rogers, *U.S. Geol. Survey, Prof. Paper*, 1921, No. **121**.

[49] J. A. Anderson, *Astrophys. J.*, 1920, **51**, 37.

[50] G. L. Wendt and C. E. Irion, *J. Amer. Chem. Soc.*, 1922, **44**, 1887; *A.*, ii, 773.

[51] *Ann. Reports*, 1920, **17**, 37.

over a platinum wire heated electrically at 800°, the effect in this case being probably due to the emission of positive ions. It is decomposed by contact with certain metals (Pt, Ni, Cu, Pb, Sb, Cd) and unchanged by others (Ag, Hg, Sn, Bi, Mo, Zn, Al). Definite proof was obtained that hydrogen contracts when activated and recovers its original volume on standing, and that the active form condenses to a liquid at or slightly above —180°. A relatively slow progressive change is observed in the spectrum produced by the discharge during the activation at —180°,[52] the Balmer series giving way to the secondary line spectrum. These results, especially the evident smallness of the energy change involved in its therm-ionic production, support the original view that this active hydrogen is in fact triatomic hydrogen, H_3 (named *hyzone*, by analogy with ozone), rather than the isotope of hydrogen, iso*hydrogen*, of atomic weight 3 (containing a *single* atomic nucleus of three protons) postulated by Harkins as a unit of atomic structure and, rather unfortunately, symbolised by him as H_3.

Wood has observed [53] that long vacuum tubes containing hydrogen give, in the central portion, mainly the Balmer series spectrum and at the ends mainly the secondary spectrum. On closing the switch, a momentary flash of the secondary spectrum, lasting about 1/50 sec., is seen throughout the tube, provided that 1/5 sec. or more has elapsed since the previous discharge. With dry hydrogen, no Balmer series is seen unless a momentary heavy condenser discharge is passed. Gas drawn by a pump from the central portion of the tube and caused to impinge upon fractured glass surfaces (or some metals, oxides, and other substances), raises them to incandescence.[54] The explanation advanced is that molecular hydrogen (to which the secondary spectrum is attributed) is dissociated by the discharge to form atomic hydrogen (believed to be the source of the Balmer spectrum), the incandesence of solids being due to their acting as catalysts for the exothermic recombination of the atoms.

Clearly the phenomena observed by Wendt and by Wood are very intimately related, but further experiment is necessary to decide finally which interpretation is correct, although Wendt's seems more probable. There is a concurrence of opinion that the " clean-up " of hydrogen and nitrogen in discharge tubes is due to chemical changes.[55] Evidence has been obtained that active

[52] G. L. Wendt and R. S. Landauer, *J. Amer. Chem. Soc.*, 1922, **44**, 510; *A.*, ii, 369.

[53] R. W. Wood, *Phil. Mag.*, 1921, [vi], **42**, 729; *A.*, 1921, ii, 665.

[54] R. W. Wood, *Proc. Roy. Soc.*, 1922, [*A*], **102**, 1; *A.*, ii, 759.

[55] F. H. Newman, *Phil. Mag.*, 1922, [vi], **44**, 215; *Nature*, 1922, **109**, 749; G. L. Wendt, *ibid.*, 749; *A.*, ii, 546, 639, 639.

modifications of hydrogen and nitrogen are produced also by the action of α-rays.[56]

Measurement of the dissociation tensions has shown that lithium hydride is the most stable of all the alkali and alkaline-earth hydrides, those of calcium, strontium, and barium decreasing in stability in the order named.[57] X-Ray photographs of lithium hydride show a structure similar to that of sodium chloride, with positive lithium-ions and negative hydrogen-ions,[58] and the view that metallic hydrides are true salts, in which hydrogen acts as a halogen, is vindicated also by very ingenious and skilful experiments proving that electrolysis of a solution of calcium hydride in a fused eutectic mixture of potassium and lithium chlorides gives hydrogen at the *anode* in the quantity required by Faraday's law.[59]

Pure hydrogen peroxide is diamagnetic to a greater extent than water and therefore does not appear to contain the molecular linking characteristic of molecular oxygen : its solubility in alcohol is 18 per cent. and in ether 1 per cent.; it is insoluble in pure dry benzene. Curves of solubility for sodium chloride, sodium nitrate, and sugar in hydrogen peroxide are generally similar to those for the same substances in water and indicate a similar degree of ionisation of the salts. The curve for sodium sulphate in hydrogen peroxide differs materially from that in water, owing to the formation of the compound $Na_2SO_4, 2H_2O_2$. The halogen hydrides are apparently insoluble in the peroxide, but are oxidised thereby ; and the halogens are much less soluble than in water. Investigation of the freezing-point curve for the system $NH_3-H_2O_2$ up to a concentration of 60 per cent. of ammonia shows the existence of one compound only, NH_3, H_2O_2, m. p. 24·5°, which can be prepared also by the action of ammonia on the peroxide in anhydrous ether. Hydrogen peroxide is quite stable in the absence of water, but its decomposition is, of course, autocatalytic.[60]

Lithium nitrate, with a little water, is a good absorbent for ammonia, and the resulting liquid, unlike those produced with ammonium nitrate or thiocyanate, has no corrosive action on steel or iron.[61]

Fused caustic soda contains about 1·1 per cent. of water, which can only be removed by heating at 500° in a vacuum. The action

[56] F. H. Newman, *Phil. Mag.*, 1922, [vi], **43**, 455; *A.*, ii, 279.

[57] F. Ephraim and E. Michel, *Helv. Chim. Acta*, 1921, **4**, 900; *A.*, ii, 58.

[58] J. M. Bijvoet and A. Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 26; *A.*, ii, 599.

[59] D. C. Bardwell, *J. Amer. Chem. Soc.*, 1922, **44**, 2499; *A.*, 1923, ii, 20.

[60] O. Maass and W. H. Hatcher, *ibid.*, 2472; *A.*, 1923, ii, 21.

[61] R. O. E. Davis, L. B. Olmstead, and F. O. Landstrum, *ibid.*, 1921, **43**, 1575, 1580; *A.*, ii, 56, 49.

upon iron, nickel, and copper of fused caustic soda, with and without the addition of 5—10 per cent. of sodium peroxide, has been studied at 350—720°; the results are very complex and interesting, many definite crystalline products having been obtained. That obtained from iron forms transparent red hexagonal crystals, stable to boiling water or aqueous caustic soda and to cold dilute mineral acids, but apparently decomposing when kept; analysis gave the composition $Na_2Fe_3O_6$, and there is some evidence that a similar compound is formed with nickel.[62]

Sodium sulphate tetrahydrate, $Na_2SO_4,4H_2O$, otherwise unknown, has been shown to exist in mixed crystals with sodium chromate.[63]

Experience gained in the preparation of free tetraethylammonium has led to the preparation of free ammonium in about a 50 per cent. yield by the addition of a 1·8 per cent. solution of potassium in liquid ammonia to a 1 per cent. ammonia solution of ammonium chloride at —70°.[64]

Rubidium bromate, prepared from the pure carbonate and bromic acid and recrystallised, forms, like cæsium bromate, small hexagonal crystals resembling cubes, m. p. 430°, and sparingly soluble in water.[65]

Measurement over a range of temperatures of the dissociation pressures of hydrated cupric alkali sulphates, of the type $CuSO_4$, $M^I_2SO_4,6H_2O$, showed the stability at any given temperature to increase in the order K, Rb, Tl, NH_4, Cs; and it is inferred that the basicity of the corresponding hydroxides increases in the same order.[66]

Excess of hydrogen peroxide gives with cold solutions of sodium copper carbonate a gelatinous, yellowish-brown precipitate having an oxygen : copper ratio between Cu : $1\frac{1}{2}$O and Cu : 2O, thus affording fresh evidence for the existence of an unstable peroxide, CuO_2.[67] The action of potassium persulphate on cuprous hydroxide in presence of barium hydroxide below 0° is said to give the oxide Cu_2O_3 which, whilst an oxidising agent, is apparently not peroxidic.[68]

Cuprous sulphide is formed by the action of sulphur on cuprous chloride.[69] Cupric sulphide on oxidation by air yields free sulphur

[62] T. Wallace and A. Fleck, *T.*, 1921, **119**, 1839.

[63] T. W. Richards and W. B. Meldrum, *J. Amer. Chem. Soc.*, 1921, **43**, 1543; *A.*, ii, 54.

[64] H. H. Schlubach and F. Ballauf, *Ber.*, 1921, **54**, [B], 2825; *A.*, ii, 55.

[65] H. D. Buell and C. R. McCrosky, *J. Amer. Chem. Soc.*, 1921, **43**, 2031; *A.*, ii, 146.

[66] R. M. Caven and J. Ferguson, *T.*, 1922, **121**, 1406.

[67] J. Aldridge and M. P. Applebey, *ibid.*, 238.

[68] G. Scagliarini and G. Torelli, *Gazzetta*, 1921, **51**, ii, 225; *A.*, ii, 68.

[69] F. W. Pinkard and W. Wardlaw, *T.*, 1922, **121**, 1300.

if freshly precipitated, but only cupric sulphate and thiosulphate if preserved for some hours before exposure to oxygen; the existence of two modifications, formulated as $Cu^{II}S$ and $Cu^{I}_2S_2S$, is inferred.[70]

The corrosion of copper by ammonium nitrate and ammonia has been found to yield cupric tetrammine nitrate and nitrite, and the preparation of the latter compound from basic cupric nitrite and ammonia is described. Dry cupric tetrammine nitrate is remarkably stable, retaining its ammonia at 120° in a vacuum, but exploding at 212° : the nitrite loses ammonia at 95—100° in air, forming the diammine nitrite, $Cu(NH_3)_2(NO_2)_2$.[71]

A strong solution of sodium persulphate (preferable to the potassium salt because of its greater solubility) acts on finely divided crystalline silver or concentrated aqueous silver nitrate to give a black peroxide which, in the latter case, gave an atomic ratio O/Ag as high as 1·295 and therefore was possibly impure Ag_3O_4.[72]

In sharp contrast with a number of doubtful or negative results,[73] Hartung, using a Steele and Grant type B quartz micro-balance [74] carrying 43 mg. and sensitive to 2×10^{-5} mg., has shown that films of silver chloride, bromide, or iodide, formed by direct halogenation of silver films, deposited from a tartrate silvering solution on thin silica supports, are darkened on exposure to light and lose weight, in some experiments with the chloride to the extent of more than 80 per cent. of the halogen present in the salt. Decomposition was accelerated in a vacuum or by presence of ozone, and rehalogenation restored the original weight and colour.[75] It seems clear, therefore, that neither oxygen nor water is essential to light action on the silver halides, and that their decomposition yields metal and halogen, and not a sub-halide.

Adsorption of iodine from aqueous or alcoholic solution does not occur with pure silver iodide,[76] and Carey Lea's observation to the contrary was probably due to the presence of silver nitrate as an

[70] W. Gluud, Ber., 1922, 55, [B], 952, 1760; A., ii, 446, 572.

[71] H. Bassett and R. G. Durrant, T., 1922, 121, 2630.

[72] G. I. Higson, ibid., 1921, 119, 2048.

[73] A. G. Rabinovich, J. Physical Chem., 1922, 26, 577; C. Tubandt and G. Eschenhagen, Z. physikal. Chem., 1922, 100, 489; J. Eggert and W. Noddack, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1921, 631; F. Weigert and W. Schöller, ibid., 1921, 641; P. P. Koch and F. Schrader, Z. Physik, 1921, 6, 127; A., ii, 606, 346, 9, 10, 183.

[74] E. J. Hartung, Phil. Mag., 1922, [vi], 43, 1056; A., ii, 495.

[75] Idem., T., 1922, 121, 682.

[76] F. E. E. Germann and R. N. Traxler, J. Amer. Chem. Soc., 1922, 44, 460; A., ii, 371.

impurity in his silver iodide. Silver perchlorate is extremely soluble in water and moderately soluble in benzene, and the three components form a remarkable system which has been studied up to the melting point of silver nitrate; silver perchlorate and water have the lowest eutectic point known for a true salt and water, $-50\cdot2°$; and a hydrate, $AgClO_4,H_2O$, and a compound, $AgClO_4,C_6H_6$, have been isolated.[77] Silver bromate is dimorphous, forming tetragonal crystals below and hair-like crystals above the transition point, $98\cdot5°$; the dry salt melts at 308—310° and is stable to light; it may advantageously be substituted for arsenious oxide as a standard in iodometry.[78] The existence of colourless and yellow forms of alkali silver thiosulphates is confirmed, and several new compounds of this type are described.[79]

A number of new, complex gold chlorides containing ammonium, rubidium, and cæsium have also been prepared.[80] Anodic oxidation of gold in dilute sulphuric acid is shown to yield auric hydroxide.[81] Hydrogen sulphide in excess reacts with very dilute aqueous chloro-auric acid to give pure auric sulphide, but the sulphides Au_2S and Au_2S_2 could not be obtained.[82]

The existence of reaction limits in gold alloys previously reported [83] has been confirmed by electrochemical investigations,[84] and Tammann's explanation, although subject to criticism, still appears the most probable.[85]

Group II.

A comparison of the band spectrum of glucinum with that of aluminium confirms the close similarity of atomic structure for these metals which would be anticipated from their chemical relationship.[86]

Glucinum hydroxide precipitated from the sulphate by ammonia is found always to contain much ammonium sulphate, which cannot

[77] A. E. Hill, *J. Amer. Chem. Soc.*, 1922, **44**, 1163; *A.*, ii, 555.

[78] J. H. Reedy, *ibid.*, 1921, **43**, 1440; *A.*, ii, 56.

[79] E. Jonsson, *Ber.*, 1921, **54**, [*B*], 2556; *A.*, ii, 57.

[80] E. Suschnig, *Monatsh.*, 1921, **42**, 399; *A.*, ii, 514; H. L. Wells, *Amer. J. Sci.*, 1922, **3**, [v], 257, 315, 414; *A.*, ii, 449, 449, 514.

[81] F. Jirsa and O. Buryánek, *Chem. Listy*, 1922, **16**, 189; *A.*, ii, 713.

[82] A. Gutbier and E. Dürrwächter, *Z. anorg. Chem.*, 1922, **121**, 266; *A.*, ii, 513.

[83] *Ann. Reports*, 1919, **16**, 198.

[84] G. Tammann, *Z. anorg. Chem.*, 1921, **118**, 48, 93; 1922, **121**, 193; R. Lorenz, W. Fraenkel, and M. Wormser, *ibid.*, 1921, **118**, 231; *A.*, ii, 75, 380, 63, 21.

[85] G. Masing, *Z. anorg. Chem.*, 1921, **118**, 293; W. H. Creutzfeldt, *ibid.*, 1922, **121**, 25; W. Jenge, *ibid.*, 1921, **118**, 36; G. Tammann, *Z. Elektrochem.*, 1922, **28**, 36; *A.*, ii, 37, 347, 64, 255.

[86] L. C. Glaser, *Ann. Physik*, 1922, [iv], **68**, 73; *A.*, ii, 675.

be washed out unless the hydroxide is first dried and powdered; when thus purified and dried, it approximates closely to the composition $Gl(OH)_2$.

The form of the 25°-isotherm for the system $GlSO_4$–$(NH_4)_2SO_4$–H_2O shows that over the range 27—30 per cent. of $GlSO_4$ and 28—37 per cent. of $(NH_4)_2SO_4$, the solid phase is the double salt, $GlSO_4$, $(NH_4)_2SO_4,2H_2O$;[87] and solubility determinations for glucinum sulphate in water indicate that $GlSO_4,4H_2O$ is the only solid phase, and that the hexahydrate previously reported is not formed.[88]

Dilute magnesium amalgam absorbs ammonia with separation of a solid solution of magnesium hexammoniate, $Mg(NH_3)_6$, in mercury;[89] and thermal analysis of the system magnesium–mercury shows the existence of the compounds $MgHg_2$, with transition at 170° to $MgHg$, m. p. 625°; Mg_3Hg_2, m. p. 562°; and Mg_2Hg, m. p. 580°.[99]

Magnesium perchlorate has been found to form a trihydrate as well as the hexahydrate previously described : it is completely dehydrated without decomposition at 250°, and the anhydrous salt has a remarkable avidity for water and has been proved to be an excellent neutral drying agent, rather slower in action than phosphoric oxide but as efficient as the latter at the ordinary temperature, capable of absorbing a greater quantity of water per unit weight, and easily regenerated by heating.[91] Evidence is adduced for the existence of magnesium sulphate octahydrate, having a transition point to the heptahydrate at 48·2°.[92]

An improved method is given for the electrolytic preparation of dilute calcium amalgam.[93] Metallic calcium gives a vapour pressure curve which, by extrapolation, indicates a boiling point of 1240°; but the metal used contained nearly 3 per cent. of impurity, including 1·62 per cent. of magnesium,[94] and it seems appropriate to repeat the protest entered in a previous Report against the use of impure or indefinite material in exact determinations. Pure calcium is found to be almost passive toward nitrogen, but the presence of more electropositive metals (K, Ba) or, better, calcium nitride favours reaction.[95]

[87] H. T. S. Britton, *T.*, 1922, **121**, 2612.

[88] *Idem., ibid.*, 1921, **119**, 1967.

[89] A. G. Loomis, *J. Amer. Chem. Soc.*, 1922, **44**, 8; *A.*, ii, 294.

[90] R. P. Beck, *Rec. trav. chim.*, 1922, **41**, 353; *A.*, ii, 545.

[91] H. H. Willard and G. F. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2255; *A.*, ii, 850.

[92] S. Takegami, *J. Chem. Soc. Japan*, 1921, **42**, 441; *A.*, 1921, ii, 698.

[93] B. S. Neuhausen, *J. Amer. Chem. Soc.*, 1922, **44**, 1445; *A.*, ii, 643.

[94] N. B. Pilling, *Physical Rev.*, 1921, **18**, 362; *A.*, ii, 291.

[95] O. Ruff and H. Hartmann, *Z. anorg. Chem.*, 1922, **121**, 167; O. Ruff, *Z. physikal. Chem.*, 1922, **100**, 419; *A.*, ii, 377, 363.

The existence of solid calcium–ammonium at $-15°$ to $+30°$ is confirmed;[96] and new compounds of calcium chloride with 1 mol. of ammonia and of calcium bromide and iodide with 1, 2, and 8 molecules of ammonia have been prepared, and the vapour tensions of these and the known ammines determined.[97] The second calcium silicide previously reported and variously formulated by different workers, is now shown to be calcium monosilicide, CaŜi or Ca_2Si_2.[98]

Strontium is completely insoluble in solid lead, but forms one compound, Pb_3Sr, m. p. 676°, which is said to form with lead a eutectic melting at the same temperature as lead.[1]

Reaction between nitrogen in excess and compressed mixtures of barium carbonate with wood-charcoal or graphite attains a practicable velocity at 1300—1400° : in fifteen to thirty minutes at this temperature, formation of cyanide reaches a maximum of 65 per cent., which is not increased at 1600°. The primary change produces barium carbide, which then reacts with nitrogen to form cyanide; cyanamide formation is due to a secondary reaction which is facilitated by higher temperature.[2]

Barium sulphate dissolves in 98 per cent. sulphuric acid at 25° to the extent of 14·9 grams/100 c.c., and the solution contains barium sulphuric acid, $H_2[Ba(SO_4)_2]$, which can be accumulated and crystallised in the anode compartment by electrolytic transport. Barium selenic acid can be prepared in a similar manner or by crystallisation from a saturated solution of barium selenate in selenic acid.[3]

Thermal analysis shows the zinc–arsenic alloys to comprise two brittle compounds, Zn_3As_2, m. p. 1015°, and $ZnAs_2$, m. p. 771°;[4] and indicates that magnesium and cadmium form one compound, CdMg, soluble in all proportions in either metal.[5]

Cadmium dissolves in aqueous ammonium nitrate quietly and without evolution of gas, and it has thus been proved that impurities in the metal form a net-like structure between the crystallites.[6]

Tests of the method previously described[7] for the purification of mercury by air at 150° showed that it removed lead completely

[96] E. Botolfsen, *Bull. Soc. chim.*, 1922, [iv], **31**, 561; *A.*, ii, 570.

[97] G. F. Hüttig, *Z. anorg. Chem.*, 1922, **123**, 31; *A.*, ii, 849.

[98] L. Wöhler and F. Müller, *ibid.*, 1921, **120**, 49; *A.*, ii, 293.

[1] E. Piwowarsky, *Z. Metallk.*, 1922, **14**, 300; *A.*, ii, 644.

[2] P. Askenasy and F. Grude, *Z. Elektrochem.*, 1922, **28**, 130; *A.*, ii, 445.

[3] J. Meyer and W. Friedrich, *Z. physikal. Chem.*, 1922, **101**, 498; *A.*, ii, 644.

[4] W. Heike, *Z. anorg. Chem.*, 1921, **118**, 264; *A.*, ii, 60.

[5] L. Guillet, *Rev. Met.*, 1922, **19**, 359; *A.*, ii, 570.

[6] G, Tammann, *Z. anorg. Chem.*, 1922, **131**, 275; *A.*, ii, 502.

[7] *Ann. Reports*, 1921, **18**, 45.

with a loss of 2 per cent. of mercury as against a loss of 3·7 per cent. when purification was effected in the usual way with nitric acid (d 1·175), but that tin was not completely eliminated by fifteen hours' air treatment (loss 1·4 per cent.) or by three passages through nitric acid (loss 9·2 per cent.).[8] A study of the equilibrium between mercuric chloride, yellow mercuric oxide, and water at 35° shows the existence of two oxychlorides of mercury; $HgCl_2,2HgO$, forming purplish-scarlet needles, and $HgCl_2,4HgO$, a brownish-yellow amorphous substance which appears to form a solid solution with mercuric oxide.[9]

Group III.

The potassium salt of hexahydrodioxydiboron has been isolated. Magnesium boride is extracted with dilute aqueous potassium hydroxide, the extract is concentrated in a vacuum, separated from potassium metaborate and magnesium hydroxide and further concentrated, and the residue is washed with methyl alcohol and recrystallised two or three times in a vacuum from water free from carbon dioxide. It forms slightly deliquescent, colourless crystals, easily soluble in water. The solution has an alkaline reaction, is a powerful reducing agent, and yields hydrogen when acidified and even, slowly, on exposure to atmospheric carbon dioxide; concentrated nitric acid acts upon the solid salt so vigorously that the hydrogen evolved takes fire. The salt in solution evolves 2·95 per cent. of its weight of hydrogen; the residual solution can further absorb 1 atom of iodine for each two atoms of hydrogen previously evolved; and measurements of equivalent conductivity indicate that the molecular formula is $K_2O_2B_2H_4$.[10] The properties of the salt thus confirm the earlier view [11] that aqueous extracts of magnesium boride contain the acid $H_6B_2O_2$, to which the structural formula (I) is attributed because it best represents the loss of hydrogen to form (II) and the subsequent interaction with iodine (III).

$$\text{(I.)} \quad \begin{matrix} H_2{:}B{\cdot}OH \\ \| \\ H_2{:}B{\cdot}OH \end{matrix} \quad \xrightarrow{-2H_2} \quad \text{(II.)} \quad \begin{matrix} B{\cdot}OH \\ \| \\ B{\cdot}OH \end{matrix} \quad \xrightarrow{+I_2} \quad \text{(III.)} \quad \begin{matrix} B{\cdot}O \\ \| \, | \\ B{\cdot}O \end{matrix}$$
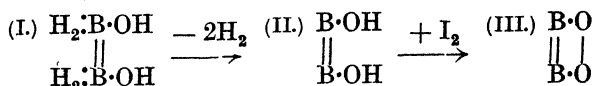
In the course of attempts to prepare complex polyborates, the pentaborates of potassium, rubidium, and thallium, $M^I_2O,5B_2O_3$, crystallising with 8, 10, and $8H_2O$, respectively, have been prepared.[12]

Crystalline aluminium hydroxide, identical under X-ray examination with the mineral *gibbsite*, begins to decompose only at 145° and

[8] C. Harries and F. Evers, *Z. angew. Chem.*, 1921, **34**, 541; *A.*, 1921, ii, 698.

[9] S. Toda, *J. Chem. Soc. Japan*, 1922, **43**, 312; *A.*, ii, 769.

[10] R. C. Rây, *T.*, 1922, **121**, 1088.

[11] Of Travers, Rây, and Gupta.

[12] A. Rosenheim and F. Leyser, *Z. anorg. Chem.*, 1921, **119**, 1; *A.*, ii, 50.

at 200° still retains 8 per cent. of water, which is completely removed only at much higher temperatures. The product of dehydration at 275° adsorbs water, but does not combine with it. Alumina prepared by dehydration at 325° gives an X-ray pattern which indicates a structure, crystalline, but different from that of diaspore, Al_2O_3,H_2O, or corundum; the product of calcination above 1000° gives the pattern of corundum.[13]

Aluminium chlorosulphoxide, $AlCl_3,SO_2$, is obtained by agitating powdered aluminium chloride with sulphuryl chloride for eight hours at 0—30° with rigid exclusion of water; when treated with sulphur or sulphur monochloride in sulphuryl chloride solution, it yields a crystalline precipitate of the compound Al_2Cl_6,S_2Cl_2. Both compounds are violently decomposed by water, in the latter case with separation of free sulphur, and are extremely active agents for the chlorination of organic compounds.[14]

It has been found that hydrochloric and sulphuric acids do not, as has been supposed, reduce thallic oxide, but dissolve it to form the corresponding thallic salts. The existence of an acid (or mixed) sulphate, with a ratio $Tl : SO_4 = 1 : 2$, has been confirmed; and the reduction of thallic salts by hydroxylamine, ferrous sulphate, and sodium arsenite has been found to proceed according to the equations $Tl_2O_3 + 2NH_2 \cdot OH \rightarrow Tl_2O + 3H_2O + N_2O$; $Tl_2(SO_4)_3 + 4FeSO_4 \rightarrow 2Tl_2SO_4 + 2Fe_2(SO_4)_3$; $Tl_2O_3 + As_2O_3 \rightarrow Tl_2O + As_2O_5$.[15] There is reason to believe that $Tl_2SO_4,Tl_2(SO_4)_3$ and $5Tl_2SO_4,Tl_2(SO_4)_3$ are the only thallous-thallic sulphates which exist.[16]

Thermal analysis of the system $Tl_2O–B_2O_3$ indicates the existence of thallous ortho-, meta-, and pyro-borates, the first melting at 370° with decomposition and the others melting at about 474° and 434°, respectively.[17] Double halides of thallium and bismuth, $2TlBr,BiBr_3$ and $2TlI,BiI_3$, precipitated by potassium bromide or iodide from nitric acid solutions of the constituent metals, form respectively lemon-yellow and red hexagonal crystals, readily hydrolysed to thallous halide, bismuth oxyhalide, and free halogen;[18] and some double thiosulphates of thallium and arsenic, antimony, or bismuth, of the type $Tl_3M(S_2O_3)_3$,[19] and complex or

[13] L. H. Milligan, *J. Physical Chem.*, 1922, **26**, 247; *A.*, ii, 447.

[14] O. Silberrad, *T.*, 1922, **121**, 1015.

[15] A. J. Berry, *ibid.*, 394.

[16] A. Benrath and H. Espenschied, *Z. anorg. Chem.*, 1922, **121**, 361; *A.*, ii, 504.

[17] G. Canneri and R. Morelli, *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 109; *A.*, ii, 571.

[18] G. Canneri and G. Perina, *Gazzetta*, 1922, **52**, i, 241; *A.*, ii, 512.

[19] G. Canneri, *ibid.*, 37; *A.*, ii, 378.

[20] V. Cuttica and A. Paciello, *ibid.*, 141; *A.*, ii, 377.

double nitrites of thallium with copper, nickel, barium, or lead, $Tl_3[Cu(NO_2)_5]$; $Tl_4[Ni(NO_2)_6]$; $TlNO_2,2Ba(NO_2)_2$; $2TlNO_2$, $Pb(NO_2)_2,H_2O$ have been described.[20]

A careful redetermination has been made of the densities of the oxides of six rare-earth metals (La, Pr, Nd, Sm, Eu, Gd),[21] and a good deal of work, which cannot usefully be summarised here, has been done on the separation of the rare-earths by basic precipitation and kindred methods,[22] and on the extraction of scandium from thorveitite and its purification.[23]

Group IV.

The fusion of carbon at atmospheric pressure by resistance heating of carbon rods is reported : the solidified drops of carbon and the points from which they are detached are said to consist of pure graphite.[24] The observation that diamond is unchanged when heated at 1100° in carbon dioxide but becomes covered with amorphous carbon [25] would, if correct, seem to afford a possible means of preparing pure carbon without possibility of contamination with hydrogen, an attempt to obtain this by decomposition of carbon monoxide at 450° in presence of ferric oxide having failed.[26]

When aqueous carbon dioxide is added to a large excess of ammonia, the anhydrous carbon dioxide immediately forms ammonium carbamate, which is sufficiently stable to permit the precipitation of the carbonate carbon dioxide as barium carbonate. This method has been applied to a study of the hydration of carbon dioxide in solutions of sodium hydroxide and sodium carbonate.[27]

Iron pentacarbonyl is best obtained from iron and carbon monoxide at 200° and 300 atm. pressure; molybdenum carbonyl, formerly supposed to be $Mo(CO)_6$, is now found to have a Mo : CO ratio 1 : 5·2, best represented by $Mo_5(CO)_{26}$ or a similar complex formula. Two ruthenium carbonyls are obtained at 300—400 atm. pressure : one a crystalline solid of unknown composition, soluble in benzene but insoluble in alcohol or water; the other a chocolate-brown, amorphous solid, $Ru(CO)_2$, insoluble in benzene, but soluble in

[21] W. Prandtl, *Ber.*, 1922, **55**, [*B*], 692; *A.*, ii, 379.

[22] W. Prandtl and J. Rauchenberger, *Z. anorg. Chem.*, 1921, **120**, 120, 311; W. Prandtl and J. Lösch, *ibid.*, 1922, **122**, 159; P. H. M.-P. Brinton and C. James, *J. Amer. Chem. Soc.*, 1921, **43**, 1397, 1446; *A.*, ii, 298, 770, 769, 62, 39.

[23] P. Urbain and G. Urbain, *Compt. rend.*, 1922, **174**, 1310; *A.*, ii, 504.

[24] E. Ryschkewitseh, *Z. Elektrochem.*, 1921, **27**, 445; 1922, **28**, 185; compare F. Sauerwald, *ibid.*, 1922, **28**, 183; *A.*, 1921, ii, 696; 1922, ii, 443.

[25] A. Foix, *Bull. Soc. chim.*, 1922, [iv], **33**, 678; *A.*, ii, 641.

[26] J. P. Wibaut, *Rec. trav. chim.*, 1922, **41**, 400; *A.*, ii, 565.

[27] C. Faurholt, *Z. anorg. Chem.*, 1921, **120**, 85; *A.*, ii, 272.

alcohol or water without decomposition.[28] The action of nitric oxide on cobalt tetracarbonyl causes evolution of carbon monoxide and yields a cherry-red liquid which has been definitely characterised as $Co(CO)_3,NO$, $d^{14°} = 1.5126$; m. p. $- 1.05°$; b. p. $78.6°$ at 760 mm. Mol. wt. (from V.D.) $= 171.7$ (calc. $M = 173$); it decomposes slowly above $66°$. Similar actions take place with nitric oxide and nickel pentacarbonyl or diferro nonacarbonyl, but the yields were too small to enable the composition of the products to be established.[29]

Pure sugar charcoal, heated with sulphur at 400—$1000°$ at low pressures, yields a coke-like solid containing 2.0—3.5 per cent. of sulphur which is not extracted by toluene and is only partly oxidised by bromine water or removed by heating at $750°$ in hydrogen : this affords further evidence of the existence of stable solid sulphides of carbon.[30]

Investigations of the solubility in hydrofluoric acid of the varieties of silicon obtained by crystallisation from solution in molten aluminium, silver, and copper lead to the conclusion that they differ mainly in degree of subdivision and are not really allotropic forms ; [31] a view confirmed by X-ray evidence that the structures of amorphous, graphitic, and crystalline silicon are identical.[32]

Sodium metasilicate is found to yield three hydrates only : $Na_2SiO_3,9H_2O$, rhombic, m. p. $47°$; $Na_2SiO_3,6H_2O$, monoclinic, m. p. $63.5°$; and $Na_2SiO_3,4H_2O$, hexagonal, m. p. 83—$85°$, other hydrates mentioned in the literature being probably mixtures of these.[33]

Much interesting work has been done on germanium, our previous knowledge of which was due very largely to Winkler, whose investigations were limited by lack of material. Germanium has been extracted from zinc residues containing about 0.2 per cent. of Ge by processes, described in detail in the original,[34] dependent on the volatility of the chloride with steam ; in this way relatively large amounts of this very rare element have been obtained and are being utilised in a reinvestigation of its compounds.

Germanium dioxide is largely, but not wholly, reduced to metal by hydrogen at 550—$900°$; the metal reacts with pure bromine,

[28] R. L. Mond and A. E. Wallis, *T.*, 1922, **121**, 29.

[29] *Idem.*, *ibid.*, 32.

[30] J. P. Wibaut, *Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 92; *Rec. trav. chim.*, 1922, **41**, 153; *A.*, ii, 52, 373.

[31] W. Manchot, *Ber.*, 1921, **54**, [*B*], 3107; W. Manchot and H. Funk, *Z. anorg. Chem.*, 1922, **120**, 277; **122**, 22; *A.*, ii, 144, 286, 764.

[32] W. Gerlach, *Physikal. Z.*, 1922, **23**, 114; *A.*, ii, 265.

[33] A. Erdenbrecher, *Mikrokosmos*, 1921, **15**, 55; *A.*, ii, 444.

[34] L. M. Dennis and J. Papish, *J. Amer. Chem. Soc.*, 1921, **43**, 2131; *A.*, ii, 150.

superficially at the ordinary temperature, completely at 220°, to form the tetrabromide, which is best purified by fractional distillation and then forms a white solid crystallising in regular octahedra, m. p. 26·1°, b. p. (corr.) 185·9°. The liquid can be supercooled to − 18° and has $n_D^{25°} = 1·6269$, $d_{29°}^{29°} = 3·1315$, and specific conductivity $<0·000078$ mhos. The tetrachloride, similarly prepared, and freed from chlorine by prolonged passage of a current of air, is a colourless liquid, b. p. 86·5° (corr.), m. p. − 49·5°, $n_D^{27°}$ 1·3606, $d_{25°}^{25°}$ 1·874. Both compounds fume in air and are slowly decomposed by water with a characteristic crackling sound, but are unchanged by strong sulphuric acid.[35]

As an outcome of general investigations [36] on the preparation of gaseous metallic hydrides by the spark discharge and from alloys and solutions germanium hydride has been shown to have the composition GeH_4 and to be free from any considerable amount of other hydrides.[37] By a modified form of the Marsh test, the formation and decomposition of the hydride may be used as an extremely delicate test for germanium; and it may be estimated gravimetrically by precipitation as magnesium orthogermanate, $MgGeO_4$.[38]

Stannous hydroxide, prepared by precipitating aqueous stannous chloride with sodium hydroxide or ammonia, is stable in air, wet or dry, up to 110°, dissolves in acetic acid to form stannous acetate, $Sn(C_2H_3O_2)_2$, has probably the formula $3SnO_2,2H_2O$, and by keeping under water is converted into dark grey, crystalline stannous oxide, which is dispersed to a yellow, colloidal solution by excess of water.[39]

The change of α-stannic acid to β-stannic acid is explained as due to the combination of stannic hydroxide (functioning as a base) with itself (functioning as an acid), and the theory receives support from measurements of the relative strength of the hydroxide as acid and as base considered in conjunction with the solubility of the α- and β-forms in hydrochloric acid and caustic alkali, as to which new facts are adduced.[40]

The existence of lead monoxide in two forms, recently denied,[41] has been conclusively proven. By slow cooling, solutions of lead oxide in aqueous caustic potash yield, according to the concentration of alkali, relatively large crystals of either the stable red tetragonal

[35] L. M. Dennis and F. E. Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299; *A.*, ii, 302.

[36] F. Paneth *et al.*, *Ber.*, 1922, **55**, [*B*], 769, 775; *A.*, ii, 383.

[37] F. Paneth and E. Schmidt-Hebbel, *ibid.*, 2615; *A.*, ii, 776.

[38] J. H. Müller and N. H. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909; *A.*, ii, 775; J. H. Müller, *ibid.*, 2493; *A.*, 1923, ii, 43.

[39] F. W. Bury and J. R. Partington, *T.*, 1922, 121, 1998.

[40] G. E. Collins and J. K. Wood, *ibid.*, 441, 1122, 2760.

[41] S. Glasstone, *ibid.*, 1921, **119**, 1914.

form or the metastable yellow rhombic bipyramidal form; and these forms differ in density, in solubility, and in $E.M.F.$ against lead in normal caustic soda.[42] There is some evidence that these forms are enantiotropic; but this point is in doubt, and further investigation is required to establish their relationship. Further physical investigation of the oxides of lead confirms the view of red lead as plumbous orthoplumbate and indicates the probable existence of a higher oxide in electrolytically deposited lead dioxide.[43]

Examination of the X-ray spectra of rare-earth oxides has identified Urbain's celtium as the element of atomic number 72, intermediate between lutecium, 175, and tantalum, 181·5, and a member of this group.[44]

Group V.

Formation of ammonia in good yield from hydrogen and excess of nitrogen in electron tubes occurs with applied electromotive forces equal to or greater than the ionisation potential of nitrogen; [45] which is held to show that ionisation of nitrogen is the first step in this synthesis.

Decomposition of ammonium nitrate proceeds normally at 210—260°, yielding 98 per cent. nitrous oxide, but the presence of even 0·1 per cent. of ammonium or sodium chloride, or the over-heating of the pure nitrate, gives impure gas containing 30—50 per cent. of nitrogen; with the pure salt, the subsidiary reactions are probably $NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$ and $5NH_3 + 3HNO_3 \longrightarrow 9H_2O + N_2$, and the explosive decomposition at 300° may be represented as $8NH_4NO_3 \longrightarrow 16H_2O + 2NO_2 + 4NO + 5N_2$.[46] Ammonium chlorate is perfectly stable in cold saturated aqueous solutions, but if solid salt is present progressive decomposition occurs which finally becomes explosive; the solid decomposes, rapidly if enclosed, slowly if exposed, the residue being ammonium nitrate free from chloride. These phenomena are due to autoxidation, catalysed by the products of decomposition.[47]

A simple method has been described for the preparation of crystalline hydroxylamine by interaction of equivalent quantities of the hydrochloride and sodium ethoxide in absolute alcohol;

[42] M. P. Applebey and R. D. Reid, $T.$, 1922, **121**, 2129; see also F. M. Jaeger and H. C. Germs, $Z.$ $anorg.$ $Chem.$, 1921, **119**, 145; $A.$, ii, 65.

[43] S. Glasstone, $T.$, 1922, **121**, 58, 1456, 1469, 2091.

[44] A. Dauvillier, $Compt.$ $rend.$, 1922, **174**, 1347; $A.$, ii, 463; G. Urbain, $ibid.$, 1349; $A.$, ii, 505.

[45] E. B. Andersen, $Z.$ $Physik$, 1922, **10**, 54; E. Hiedmann, $Chem.$ $Ztg.$, 1921, **45**, 1073; $A.$, ii, 562; $A.$, 1921, ii, 694.

[46] H. L. Saunders, $T.$, 1922, **121**, 698.

[47] F. Fairbrother, $J.$ $Amer.$ $Chem.$ $Soc.$, 1922, **44**, 2419; $A.$, 1923, ii, 27.

the product differs from the purest hydroxylamine hitherto obtained only in being rather less stable.[48]

The mechanism of absorption of oxides of nitrogen by alkali is still in doubt; further evidence supports the view that oxidation of nitric oxide to nitrogen tetroxide proceeds without intermediate formation of nitrous anhydride; yet the absorption of a gaseous system $NO-NO_2$ by alkali hydroxide proceeds in a manner which can best be explained by assuming the presence of nitrous anhydride in small concentrations.[49] The fact that nitrogen pentoxide has unusual stability in presence of traces of ozone [50] is best explained by the assumption that its decomposition is catalysed by the products (which are reconverted immediately to pentoxide by ozone), as has been shown to be the case in the photochemical decomposition of nitrogen pentoxide and in the thermal decomposition of its solutions in carbon tetrachloride and chloroform.[51]

Evidence of the existence of an active form of hypophosphorous acid is again obtained from a study of its rate of reaction with cupric chloride; but any purely physical explanation [52] is rejected in favour of the idea that there may exist an equilibrium between the ordinary acid and its tervalent form, $HP(OH)_2$, which would be expected to be very reactive.[53]

Two interesting methods are described for the purification of phosphoric oxide, hitherto a very tedious and wasteful operation, very necessary in precise work, but often omitted. In one the oxide is dropped into a rapid current of oxygen in an iron tube at 600—700°, the sublimate being condensed in a long wide glass continuation tube; 50 grams of pure oxide can thus be prepared from 100 grams of crude material in an hour.[54] The second method is ingenious and very simple : commercial phosphoric oxide is heated at 175—220° in ozonised air until fully oxidised : the product still contains, of course, any non-volatile impurity originally present, but it is free from lower oxides and is no more liable than the resublimed oxide to yield gas in high vacua. Evidence was obtained that the phosphorous oxide present in commercial phosphoric oxide reacts

[48] H. Lecher and J. Hofmann, *Ber.*, 1922, **55**, [*B*], 912; *A.*, ii, 442.

[49] E. Briner, S. Niewiazski, and J. Wiswald, *Helv. Chim. Acta*, 1922, **5**, 432; *A.*, ii, 563; F. Foerster, *Ber.*, 1922, **55**, [*B*], 490; *A.*, ii, 284; A. Sanfourche, *Compt. rend.*, 1922, **175**, 469; *A.*, ii, 762.

[50] F. Daniels, O. R. Wulf, and S. Karrer, *J. Amer. Chem. Soc.*, 1922, **44**, 2402; *A.*, 1923, ii, 24.

[51] Daniels and Johnston, *ibid.*, 1921, **43**, 53; R. H. Lueck, *ibid.*, 1922, **44**, 757; *A.*, ii, 433.

[52] *Ann. Reports*, 1921, **18**, 41.

[53] A. D. Mitchell, *T.*, 1922, **121**, 1624.

[54] G. I. Finch and R. H. K. Peto, *ibid.*, 692.

with water to form phosphine which, under the influence of electrical discharges (for example, produced by friction between mercury and glass), reacts with mercury to form the phosphide (Hg_3P_2?) and hydrogen.[55]

Phosphine, with but little hydrogen, is best prepared by the action of 10 per cent. sulphuric acid on aluminium phosphide.[56]

A review of the past evidence and consideration of new experiments on the heat evolved by arsenic in cooling from various high temperatures confirm the transition point to yellow arsenic at about 750°, but indicates that whilst brown or "amorphous" arsenic may be, as has been supposed, a distinct monotropic modification, "grey" arsenic is probably not an allotropic form, but merely an intermediate stage in the conversion of colloidal arsenic to the crystalline state.[57] This is clearly a case in which X-ray analysis might give important information.

Arsenic combines with aluminium at 750° to give a brown, amorphous compound, Al_3As_2, infusible and undissociated at temperatures up to 1600°, but apparently dissociating at the ordinary temperature, as old specimens slowly deposit yellow arsenic and leave a residue of black arsenic on solution in hydrochloric acid, whereas the freshly prepared substance is completely soluble in acid.[58]

Bismuth subiodide, BiI_2, has been obtained in red, orthorhombic needles, which dissolve in aqueous potassium iodide to an orange solution, act as a strong reducing agent, and decompose to the tri-iodide and bismuth at 400°.[59]

It has been stated that tantalum pentachloride is a good conductor whilst columbium pentachloride is an insulator, but measurements with the anhydrous chlorides show that the conductivities are about the same and extremely small, about 0.25×10^{-6} mhos.[60]

Group VI.

Liquid ozone and oxygen are only partly miscible, and are readily separated by fractional distillation. Pure ozone so obtained has been employed for a redetermination of physical constants (m. p. $- 249.7°$; b. p. $- 112.4°$; $T_k - 5°$; P_k 64.8 atm.; d^{-182} 1.71),[61] and for an ingenious and skilful determination of vapour density

[55] J. J. Manley, *T.*, 1922, **121**, 331.

[56] L. Moser and A. Brukl, *Z. anorg. Chem.*, 1921, **121**, 73; *A.*, ii, 393.

[57] P. N. Laschtschenko, *T.*, 1922, **121**, 972.

[58] Q. A. Mansuri, *ibid.*, 2272.

[59] H. G. Denham, *J. Amer. Chem. Soc.*, 1921, **43**, 2367; *A.*, ii, 218.

[60] W. Biltz and A. Voigt, *Z. anorg. Chem.*, 1921, **120**, 71; *A.*, ii, 302.

[61] E. H. Riesenfeld and G. M. Schwab, *Ber.*, 1922, **55**, [B], 2088; *A.*, ii, 637; *Z. Physik*, 1922, **11**, 12; *A.*, ii, 761.

by direct weighing of a bulb filled with ozone, the pressure at the time of filling being extrapolated from the observed growth of pressure in the bulb after weighing. The molecular weight found confirms the formula O_3,[62] and neither investigation affords any evidence whatever of the existence of higher polymerides of oxygen.

Ozone oxidises nitrogen tetroxide instantly to the pentoxide, the completion of the quantitative reaction $N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2$ being sharply indicated by disappearance of colour, so that a true *titration* can thus be performed in the gaseous phase.[63]

Sulphur dioxide partly oxidises cuprous chloride in concentrated hydrochloric acid according to the equation (i) $2Cu_2Cl_2 + SO_2 + 4HCl \rightleftharpoons 4CuCl_2 + 2H_2O + S$; but the reverse change is obscured by a secondary action, (ii) $6CuCl_2 + S + 4H_2O \longrightarrow 3Cu_2Cl_2 + 6HCl + H_2SO_4$. With increasing acid concentration, first cuprous sulphide, then mixtures of the sulphide and sulphur, and finally sulphur only are precipitated. A reaction analogous to (i) occurs with mercurous chloride in hydrochloric acid concentrations from $8N$ to $2N$, whilst further reduction occurs (a) to mercurous chloride and mercury at $2N - 0.16N$, and (b) to mercury only at acid concentrations less than $0.02N$.[64]

Sodium sulphite or bisulphite, dropped into warm dilute aqueous sulphuric acid, yields hydrogen sulphide, probably by the reaction $4H_2SO_3 \longrightarrow H_2S + 3H_2SO_4$, which may well be an intermediate stage in the known reaction $3H_2SO_3 \longrightarrow 2H_2SO_4 + H_2O + S$;[65] and there is evidence that hydrated sodium sulphite, excluded from air, undergoes autoxidation to sulphate.[66]

Freshly prepared solutions of bisulphites show an absorption band characteristic of metabisulphites and therefore probably contain a small proportion of the latter in equilibrium; they are stable in light if oxygen is excluded, but in its presence are oxidised with formation of sulphate and develop an absorption band characteristic of hydrated sulphur dioxide.[67]

Measurements of viscosity, conductivity, and contraction on mixing show that a complex, $H_2SO_4,H_2O,(C_2H_5)_2O$, is present in systems of sulphuric acid, water, and ether.[68]

Aluminium selenide, Al_2Se_3, easily prepared from its elements

[62] S. Karrer and O. R. Wulf, *J. Amer. Chem. Soc.*, 1922, **44**, 2391.

[63] O. R. Wulf, F. Daniels, and S. Karrer, *ibid.*, 2398; *A.*, 1923, ii, 23.

[64] W. Wardlaw and F. W. Pinkard, *T.*, 1921, **121**, 210; L. M. Stewart and W. Wardlaw, *ibid.*, 1481.

[65] G. M. Bennett, *ibid.*, 1922, **121**, 1794.

[66] S. L. Shenefield, F. C. Vilbrandt, and J. R. Withrow, *Chem. and Met. Eng.*, 1921, **25**, 953; *A.*, ii, 45.

[67] E. C. C. Baly and R. A. Bailey, *T.*, 1922, **121**, 1813.

[68] J. R. Pound, *ibid.*, 941.

as a light brown powder, unstable in air, affords, by reaction with acids, a convenient source of hydrogen selenide, which can be purified by liquefaction at $-80°$ and re-evaporation. The dry gas is stable in ordinary daylight and unaffected by dry oxygen.[69] Hydrogen telluride has been prepared in a similar way and resembles the selenide except in its lesser stability to light and oxidation.[70] Further work is recorded on the properties of selenium oxychloride,[71] and the oxybromide has been obtained, by the action of bromine on a mixture of selenium and selenium dioxide at $0°$, as a reddish-yellow solid, m. p. $41·5°$, b. p. $217°/740$ mm. with much decomposition, $d^{50°}$ $3·38$, which generally resembles the oxychloride in its remarkable chemical activity.[72]

A convenient method is described for the preparation of selenium dioxide by combustion of selenium in oxygen containing nitrous fumes;[73] and it has been shown that it forms only one hydrate, SeO_2,H_2O.[74] Nitrosylselenic acid, $NO·O·SeO_2·OH$, obtained by the action of liquid nitrogen trioxide on anhydrous selenic acid, is a colourless, crystalline solid melting at $80°$ with decomposition and unstable even at the ordinary temperature.[75]

Tellurium, purified by distillation and crystallised by solidification or sublimation, has d $6·310$, which is unchanged by long heating at various temperatures. It is probable, therefore, that tellurium does not exhibit the dynamic allotropy which has been attributed to it.[76] Oxidation of tellurium tetrachloride with chlorine is a convenient method of obtaining pure telluric acid in almost theoretical yield.[77]

A study of the solubility of chromium trioxide in sulphuric acid[78] shows that when the concentration of the latter is 85—95 per cent. the solid phase is brown, minutely crystalline CrO_3,SO_3; whilst in stronger acid the solid phase is probably the chromisulphuric acid, CrO_3,SO_3,H_2O, described by Gay-Lussac and recently prepared, together with the corresponding chromiselenic acid and certain salts of these acids.[79]

[69] L. Moser and E. Doctor, *Z. anorg. Chem.*, 1921, **118**, 284; *A.*, ii, 46.

[70] L. Moser and K. Ertl, *ibid.*, 269; *A.*, ii, 48.

[71] V. Lenher, *J. Amer. Chem. Soc.*, 1922, **44**, 1664; *A.*, ii, 706; compare *Ann. Reports*, 1921, **18**, 53.

[72] *Idem., ibid.*, 1668; *A.*, ii, 707.

[73] J. Meyer, *Ber.*, 1922, **55**, [B], 2082; *A.*, ii, 639.

[74] W. Manchot and K. Ortner, *Z. anorg. Chem.*, 1922, **120**, 300; *A.*, ii, 283.

[75] J. Meyer and W. Wagner, *Ber.*, 1922, **55**, [B], 690; *A.*, ii, 372.

[76] A. Damiens, *Compt. rend.*, 1922, **174**, 1344, 154C; *A.*, ii, 498, 562.

[77] J. Meyer and H. Moldenhauer, *Z. anorg. Chem.*, 1921, **119**, 132; *A.*, ii, 49.

[78] L. F. Gilbert, H. Buckley, and I. Masson, *T.*, 1922, **121**, 1934.

[79] J. Meyer and V. Stateczny, *Z. anorg. Chem.*, 1922, **122**, 1; *A.*, ii, 773.

The dichlorides of molybdenum, tungsten, and tantalum have been prepared, in some cases by new methods, and have been shown uniformly to be represented by the formula $HM_3Cl_7,4H_2O$ and not by the complex formulæ hitherto given to them.[80]

Metallic tungsten acts slowly on thoria at 2400° in a vacuum and in argon, nitrogen, or hydrogen to form thorium and tungsten trioxide, the latter appearing in part to react with tungsten to form a grey, metallic, crystalline substance, very stable to acids and alkalis, which may be a " bronze " of the type $Th(WO_3)_n$, where $n = 3 - 10$.[81]

The green colour sometimes observed in tungsten trioxide is due to surface reduction to lower oxides,[82] and X-ray examination of the hydrated oxides shows the existence of H_2WO_4 and H_4WO_5 as distinct compounds,[83] the former being confirmed also by the form of the vapour pressure–composition curve.[84] Evidence has been obtained that the sodium tungstate, $4Na_2O,10WO_3,23H_2O$, is really an acid salt, $4(Na_2WO_4),6(H_2WO_4),17H_2O$, and corresponding salts of other bases, differing, however, in water content, have been isolated.[85]

An icositetrahydrate of uranyl nitrate, $UO_2(NO_3)_2,24H_2O$, is found to exist at temperatures below $- 20°$.[86]

Group VIII.

The photography of the spectrum of fluorine, excited by the discharge between gold electrodes, deserves mention because of the attendant experimental difficulties.[87] A simple method for the preparation of pure ammonium hydrogen fluoride consists in treating aqueous hydrofluosilicic acid with excess of ammonia, filtering, concentrating in platinum, and subliming the product.[88]

The existence of $HClBr_2$, deduced by Berthelot from the heat of solution of bromine in hydrochloric acid, is confirmed and that of $HClI_2$ and $HBrI_2$ evidenced by measurements of the distribution of free halogen between aqueous halogen acids and an immiscible solvent.[89]

The normal chlorites of sodium, lithium, calcium, strontium,

[80] K. Lindner *et al.*, *Ber.*, 1922, **55**, [B], 1458; *A.*, ii, 509.

[81] C. J. Smithells, *T.*, 1922, **121**, 2236; compare E. Wedekind, *Edel-Erden und -Erze*, 1922, **3**, 109.

[82] J. A. M. van Liempt, *Z. anorg. Chem.*, 1921, **119**, 310; *A.*, ii, 73.

[83] H. C. Burger, *ibid.*, 1922, **121**, 240; *A.*, ii, 508.

[84] G. F. Hüttig and B. Kurre, *ibid.*, 1922, **122**, 44; *A.*, ii, 773.

[85] E. F. Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027; *A.*, ii, 774.

[86] F. E. E. Germann, *ibid.*, 1466; *A.*, ii, 649.

[87] W. R. Smythe, *Astrophys. J.*, 1921, **54**, 133; *A.*, ii, 99.

[88] M. Ikawa, *J. Chem. Soc. Japan*, 1921, **42**, 768.

[89] P. Râature and P. V. Sarkar, *T.*, 1922, **121**, 1449.

and univalent thallium have been prepared and are found to be unstable substances, exploding when dry by percussion and decomposed by heat, in the case of the sodium salt according to the equation $3NaClO_2 \longrightarrow 2NaClO_3 + NaCl$.[90]

An examination of the mineral fluocerite by means of the X-ray spectrograph has given indications [91] that it may contain the element of atomic number 61, a member of this group.

Group VIII.

The amount of electrolytic iron foil dissolved by aqueous sulphuric acid (in thirty-four hours at 15°) has been found to vary with acid concentration in a remarkable manner, rising steadily with $0.5N$- to $2N$-acid, then falling with $3N$-acid, and again increasing to progressively higher values with $4N$- and $5N$-acid. Another series of experiments shows that when a disk of pure iron is rotated for thirty minutes in acids of concentrations $N/5$, $N/10$, $N/50$, and $N/100$, the amount of iron dissolved depends only on the velocity of rotation, with which it increases linearly up to a peripheral speed of 35 m.p.h., in marked contrast to the corrosion of iron in aerated water, which ceases at a speed of 5 m.p.h.[92]

Samples of ferric oxide prepared by twenty-seven different methods have been found to give identical X-ray spectra, which affords strong evidence that, despite their outward differences, they are really the same form of the compound.[93] A peculiar iron salt, $FeSO_4Cl,6H_2O$, has been obtained by treating a concentrated solution of ferrous sulphate with chlorine, and by other methods.[94]

It is satisfactory to record the publication of a study of the general equilibrium in the system Fe_2O_3–SO_3–H_2O from 50—200° which resolves in a convincing fashion the doubt and complexity associated with the hydrates and sulphates of ferric oxide. The components in suitable proportions were heated together in sealed tubes for times so prolonged as to ensure the attainment of equilibrium (its non-attainment being the probable cause of uncertain and conflicting results in many previous investigations of the system), and the liquid and wet solids were separated and analysed. Determination of the composition of the dry solid phase was effected by Schreinemakers's "residue" method, controlled by microscopic observations, especially of refractive index and dispersion. The results, embodied

[90] G. R. Levi, Gazzetta, 1922, 52, i, 417; Atti R. Accad. Lincei, 1922, [v], 31, i, 212, 370; A., ii, 567.

[91] A. Hadding, Z. anorg. Chem., 1922, 122, 195; A., ii, 780.

[92] J. A. Newton Friend and J. H. Dennett, T., 1922, 121, 41.

[93] J. A. Hedvall, Z. anorg. Chem., 1922, 120, 327; 121, 217; A., ii, 300, 381.

[94] O. Röhm, Collegium, 1921, No. 614, 282; A., ii, 648.

in a series of triangular diagrams and a solid model, indicate that the only solid phases existing within the range studied are : [95] Fe_2O_3 ; Fe_2O_3,H_2O ; $3Fe_2O_3,4SO_3,9H_2O$; $Fe_2O_3,2SO_3,H_2O$; $Fe_2O_3,2SO_3,5H_2O$; $2Fe_2O_3,5SO_3,17H_2O$; $Fe_2O_3,3SO_3$ (two forms : rhombohedral and orthorhombic); $Fe_2O_3,3SO_3,6H_2O$; $Fe_2O_3,3SO_3,7H_2O$; $Fe_2O_3,4SO_3,3H_2O$; $Fe_2O_3,4SO_3,9H_2O$. Other investigations confirm the existence, as phases stable in part of the system at 18° and 25°, of $Fe_2O_3,3SO_3,7H_2O$ and $Fe_2O_3,4SO_3,9H_2O$.[96] The colourless form of iron alum occasionally encountered is shown to be due to the presence of ferric hydroxide as an impurity.[97]

In the course of further studies on the properties of subsidiary valency groups, the trihydrate and tri- and hexa-ammines of cobaltous fluoride have been prepared.[98]

Aqueous solutions of ruthenium tetroxide conduct electricity, have a weak acid reaction, and form salts with alkalis ; but of these only the ammonium salt, $(NH_4)_2RuO_5$, could be obtained in a pure state.[99]

[95] E. Posnjak and H. E. Merwin, *J. Amer. Chem. Soc.*, 1922, **44**, 1965; *A.*, ii, 772.

[96] M. P. Appleby and S. H. Wilkes, *T.*, 1922, **121**, 337.

[97] J. Bonnell and E. P. Perman, *T.*, 1921, **119**, 1994.

[98] G. L. Clark and H. K. Buckner, *J. Amer. Chem. Soc.*, 1922, **44**, 230; *A.*, ii, 300.

[99] F. Krauss, *Z. anorg. Chem.*, 1921, **119**, 217; *A.*, ii, 75.

H. V. A. BRISCOE.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

THE general arrangement of the aliphatic compounds which was adopted in previous Reports has been followed in the present case, and, whilst the headings of the different sections indicate broadly the character of the compounds considered in the various groups, an arbitrary choice has sometimes to be made. Theoretical discussions based on an extended survey of reactions obviously present this difficulty to the Reporter, and it is imperative that generalisations such as those which have appeared on the induced polarity of atoms, and the interpretation of the theory of partial valencies on an electronic basis, by Lapworth and by Kermack and R. Robinson,[1] should not be relegated to any single sub-section of compounds. These authors have now reviewed their generalisations in the light of the Thomson and Lewis-Langmuir theory of the atom and of valency, and this may be regarded as a physical basis for their hypotheses. Whilst it is impossible in a sectional report to do justice to these theoretical considerations inasmuch as they cover the whole field of reactions in organic chemistry, nevertheless occasional references will be found in the succeeding pages.

Hydrocarbons.

A notable feature of the recent researches on hydrocarbons is the tendency to focus on the study of the additive reactions of the simpler unsaturated members of the group. Attention has been directed to the conditions governing the hydrogenation[2] of ethylene and acetylene in the presence of nickel or of nickel–mercury catalysts. With the latter, acetylene may be reduced at 25—35° to both a light oil consisting of ethylenic hydrocarbons and a heavier oil. In the preparation of either ethane or ethylene from acetylene, it is advantageous to dilute the acetylene with the expected products. Combination of anhydrous sulphuric acid with acetylene occurs under pressure at 0° in presence of mercuric

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[1] *T.*, 1922, **121**, 416, 427.

[2] E. K. Rideal, *T.*, 1922, **121**, 309; K. Òda, *J. Chem. Ind. Japan*, 1921, **24**, 1161; *A.*, 1921, i, 841.

sulphate [3] with the almost quantitative formation of vinylsulphuric acid, $CH_2:CH \cdot SO_3 \cdot OH$. Acetonitrile is produced at higher temperatures by combination of acetylene with ammonia, but, in presence of excess of the former, pyrrole and picoline are among the products. Similar evidence of polymerisation of a hydrocarbon during its combination with other reagents is furnished in the case of ethylene, which, under the influence of the silent discharge, unites with nitrogen to give a complex nitrile, $C_{18}H_{31} \cdot CN$.

The catalytic method for the dehydration of alcohols has been applied in a preparation of pure propylene, the physical constants of which have now been determined with accuracy.[4] It is of interest that this gaseous hydrocarbon is formed by isomeric change from *cyclo*propane at 600—700°; the reversible reaction, *cyclo*propane $\rightleftharpoons$ propylene, is thus an example of the three-carbon tautomerism which has been studied by Thorpe and his school. Consideration of the kinetics of open-chain compounds and thermochemical data accord with the view that the Baeyer strain theory as applied to double linkings is open to criticism, since it is known that an ethylenic bond is more easily formed than a five-membered ring.[5] Quite different in character is the reaction which leads, under similar conditions to the above, from ethylene to butadiene,[6] in which case a synthetic operation is involved with loss of hydrogen. The hydrocarbon synthesised from pinacolin by the application of the Grignard reagent followed by dehydration has the formula $CMe_3 \cdot CMe:CH_2$, which undergoes reduction by Paal's method to a new heptane, trimethyl*iso*propylmethane.[7] When pinacolin is chlorinated by phosphorus pentachloride, the normal dichloride is produced along with the unsaturated derivative, $CMe_3 \cdot CCl:CH_2$. Elimination of hydrogen chloride leads to a dimethylbutinene which on reduction gives rise to ββ-dimethylbutane. Physical constants of these hydrocarbons have been determined.

Separation of two geometric isomerides by fractional distillation is a simple procedure in the case of maleic and fumaric acids, but it would appear difficult of achievement with hydrocarbons. Success has, however, been attained in the separation of the two

[3] Brit. Pat. 156121 and 147067; *A.*, i, 517; *A.*, 1921, i, 852; Miyamoto, *J. Chem. Soc. Japan*, 1922, **43**, 21; *A.*, i, 418.

[4] M. Trautz and K. Winkler, *J. pr. Chem.*, 1922, [ii], **104**, 44, 53; *A.*, i, 909, 926.

[5] J. P. Wibaut, *Rec. trav. chim.*, 1922, **41**, 441; *A.*, i, 909; Wojniczi Sianozencki, *Roezniki·Chemji*, 1921, **1**, 244; *A.*, i, 330.

[6] Zanetti, Suydam, and Offner, *J. Amer. Chem. Soc.*, 1922, **44**, 2036; *A.*, i, 977.

[7] Chavanne and Lejeune, *Bull. Soc. Chim. Belg.*, 1922, **31**, 98; *A.*, i, 417; Rissegheim, *ibid.*, **62**; *A.*, i, 313.

γ-methyl-Δ^γ-pentenes obtained from methyldiethylcarbinol by dehydration with p-toluenesulphonic acid : [8]

$$Me\cdot\underset{\underset{H\cdot C\cdot Me}{|}}{C}\cdot CH_2Me \qquad Me\cdot\underset{\underset{Me\cdot C\cdot H}{|}}{C}\cdot CH_2Me$$
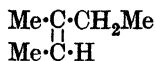
Their boiling points differ by less than 5°, and the refractive indices are distinctive. Both yield methyl ethyl ketone on oxidation, and combine additively with bromine, but hydrochloric acid effects isomerisation of one of the stereoisomerides.

Grignard reactions have been applied in improvements of recognised methods of preparing alkyl derivatives of cadmium and mercury, whilst recent investigations with metallic carbides [9] provide not only a simplified procedure for obtaining methane, but show that with superheated steam liquid products containing 60 per cent. of benzene may be collected, and by conducting the process under appropriate pressures terpenes and higher polymerised hydrocarbons are formed. On the analogy of the Würtz reaction, the anticipated result of bringing together methylene iodide and aluminium in anhydrous ether is the formation of ethylene. This conclusion is in need of verification in view of the contradictory observations of two independent workers; [10] but it seems clear that in any case the formation of ethylene or some analogue is only a secondary reaction. The chief product either from methylene bromide or iodide appears to be an interesting unsaturated type of organometallic halide, namely, $CH_2{:}AlX$, which is decomposed by water or alcohol to give methane. It combines additively with iodine, yielding a saturated compound, which also reacts with water to give methyl iodide.

Investigation of all the simpler unsaturated hydrocarbons with a view to their easy recognition is a necessary preliminary to the systematic survey of the depolymerised products of caoutchouc, and this inquiry may well run parallel with a serious study of the important phenomenon of polymerisation which, not alone in the hydrocarbon series, but also in the carbohydrate group, is a vital factor governing the constitution of the more complex natural products.

Polymerisation of vinyl chloride in ether or alcohol is promoted by extreme ultra-violet light at the ordinary temperature, and metallic salts, especially those of uranium, catalyse the reaction in sunlight. The product is a white powder which separates from

[8] Rissegheim, *Bull. Soc Chim Belg.*, 1922, **31**, 213; *A.*, i, 909.

[9] O. Ohmann, *Z. physikal. Chem. Unterr.* 1921, **34**, 76; *A.*, i, 2; Plauson and v. Tischenko, *Chem. Zentr.*, 1922, ii, 442; *A.*, i, 818.

[10] Faillebin, *Compt. rend.*, 1922, **174**, 112; *A.*, i, 119; V. Thomas, *ibid.*, 464; *A.*, i, 330.

solvents as an elastic film.[11] Hydrogenation of caoutchouc in presence of platinum leads to a product $(C_5H_{10})_x$ which remains a colloid and apparently is not depolymerised. Distillation of this product in a high vacuum yields degraded products which are simple unsaturated hydrocarbons. The results favour the theory that the caoutchouc molecule is composed of isoprene polymerised in chains of such length as to minimise their unsaturated character. The views of Harries are contested on several grounds.

Thiele's theory of the mode of attachment of addenda to a conjugated unsaturated system such as that of isoprene is supported by Staudinger and his co-workers, who have shown that both with hydrogen bromide and bromine combination occurs in the α- and δ-positions. Whether this is so under all conditions remains in doubt, since contradictory evidence is furnished by A. G. Bergmann.[12]

In the communication by Kermack and Robinson referred to in the introduction the theory of partial valencies and the attachment of addenda is interpreted on the basis of the Lewis-Langmuir hypothesis and it is shown that the usual expressions,

$$CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \quad \overset{+}{CH_2}\text{-----}CH\text{----}C\text{----}\overset{-}{CH_2}\cdots\cdots$$

become (if it is assumed on the physical basis that the symbols $=$, $\cdots$, $—$, $\cdots$, imply electrons to the number of four, three, two, and one, respectively, held in common by two atoms) the following :

$$CH_2\!\vdots\!CH\!\vdots\!CH\!\vdots\!CH_2 \qquad \overset{+}{CH_2}\!\vdots\!CH\!\vdots\!CH\!\vdots\!\overset{-}{CH_2}$$

The latter represents an extreme and unstable condition of the former non-polarised molecule, and another more stable form would be the cyclic one, such as :

$$\begin{array}{cc} CH : CH & CH\text{---}CH \\ CH_2 \cdot CH_2 & CH_2\text{---}CH_2 \end{array}$$

or
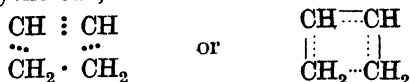
The system may be an oscillating one in which the terminal carbon atoms become in turn feebly electropositive and electronegative, the reagents taking advantage of these momentary manifestations of polarity; the process of addition is represented by an interchange of electrons of which the following is one example :

$$CH_2\!\vdots\!CH\!\vdots\!CH\!\vdots\!CH_2 \longrightarrow CH_2\!\vdots\!CH\!\vdots\!CH\!\vdots\!CH_2 \longrightarrow$$

$$\begin{array}{cc} CH_2\!\vdots\!CH\!\vdots\!CH\!\vdots\!CH_2 & CH_2\!\vdots\!CH\!\vdots\!CH\!\vdots\!CH_2 \\ \vdots Cl \vdots \quad\ Cl\vdots & \longrightarrow \quad \vdots Cl \vdots \qquad\qquad \vdots Cl \vdots \end{array}$$
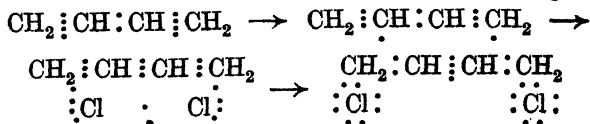
[11] J. Plotnikow, *Z. wiss. Photochem.*, 1922, **21**, 117; *A.*, i, 419; H. Staudinger and J. Fritschi, *Helv. Chim. Acta*, 1922, **5**, 785; *A.*, i, 1043.

[12] *Helv. Chim. Acta*, 1922, **5**, 743; *A.*, i, 978; *J. Russ. Phys. Chem. Soc.* 1920, **52**, 24; *A.*, i, 1106.

It is recognised, however, that other phases of interchange must be provided for to admit of alternative modes of addition under conditions such as those which lead either to trimethylene dibromide or propylene dibromide by the union of hydrogen bromide and allyl bromide, and these manifestations of " secondary conjugation " are dealt with. With a substituted system such as that which occurs in muconic acid, the attachment of hydrogen follows the Thiele rule, but bromine, on the contrary, combines in the α- and β-positions, and it is suggested [13] that the rule has been too hastily accepted as a generalisation on evidence which is restricted. It is contended that the Thiele rule should be confined to those cases of conjugation in which X and X' in the formula $XCH=CH-CH=CHX'$ are both fully saturated residues.

Experiments with petroleum reveal the disconcerting fact that polymerisation may accompany the formation of ozonides, and such considerations may have to be taken into account in evaluating the results of constitutional work undertaken with the use of ozone.[14] A study of the constituents of paraffin wax has given promising data pointing to the possibility of effecting separation of the individual hydrocarbons, but as the research is incomplete a discussion of the results may for the present be held over. The same may be said also of several investigations in which the higher paraffins have been submitted to catalytic oxidation with air or oxygen. The problem is complicated by the tendency of the normal fatty acids to undergo further oxidation to dibasic and hydroxy-acids, so that the isolation of palmitic and stearic acids may be prevented unless means can be devised to fix these primary products in such a way as to resist this tendency.

Alcohols and Derivatives.

Synthetic methods for the manufacture of methyl alcohol and formaldehyde excite the interest of all chemists, inasmuch as the demand on these raw materials extends to both pure and applied chemistry. As the two substances are so intimately related in origin, it is inadvisable to separate the reviews of several processes which claim to have achieved success in the synthesis of both or either of the products. Selection of the initial materials for the purpose must obviously depend on economic factors, and the utilisation of carbon monoxide and hydrogen is reported in two of the methods, whilst, in a third, carbon dioxide and methane are employed. The Badische process [15] is based on the conversion

[13] J. P. C. Chandrasena and C. K. Ingold, T., 1922, **121**, 1306.
[14] R. Koetschau, Z. angew Chem., 1922, **85**, 509; A., i, 977.
[15] Brit. Pat. 173097; A., i, 218.

of lithium carbonate into formate by the agency of carbon monoxide and water under pressure and at a temperature above 120°. The lithium formate is afterwards decomposed at about 400° in a current of moist hydrogen with the production of methyl alcohol and ketones, and the by-product in the first reaction is carbon dioxide. In another process,[16] purified " suction gas " or water-gas is passed rapidly over catalysts containing nickel, copper, and aluminium at 300—400° under 10 atmospheres, when it is trans-formed into formaldehyde and methane. Conversely, the oxid-ation of the latter hydrocarbon forms the basis of a third process [17] yielding both methyl alcohol and formaldehyde. By oxidation of methane at 500—700° with carbon dioxide in constricted tubes made of nickel, copper, or silver, the following reactions occur :

$$2CO_2 = 2CO + 2O; \ CH_4 + 2O = H \cdot CHO + H_2O.$$
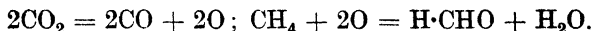
The yield of methyl alcohol is favoured by a slow passage of the mixed gases through the tubes and by introducing hydrogen into the mixture. With rapid flow of gases, however, the yield of formaldehyde amounts to 56 per cent. of the methane employed. E. W. Blair and T. S. Wheeler [18] have reinvestigated the production of formaldehyde by the circulation of mixtures of ethylene and oxygen over catalysts. By varying the conditions and the pro-portions of the mixture they were able to increase the yield of formaldehyde to 75 per cent.

Alcoholic fermentation of formaldehyde solutions is effected by osmium, and methyl alcohol and carbon dioxide are produced in the ratio of two to one, a reaction which seems to be capable of the following formulation : [19]

$$2CH_2O + H_2O \longrightarrow CH_3 \cdot OH + H \cdot CO_2H.$$
$$CH_2O + H \cdot CO_2H \longrightarrow CH_3 \cdot OH + CO_2.$$
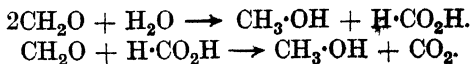
The activity of the osmium diminishes, however, rather rapidly.

Simple alcohols such as those of *iso*butyl and *iso*amyl may be prepared from the appropriate Grignard reagents [20] by the agency of hydrogen peroxide, and good yields are obtained. The character of the initial additive compounds suggests the representation of hydrogen peroxide by the formula O:OH·H at the moment of its participation in the reaction :

$$MgRX + H_2O_2 \longrightarrow H \cdot OHR \cdot OMgX \xrightarrow{H_2O} R \cdot OH + MgX \cdot OH + H_2O.$$
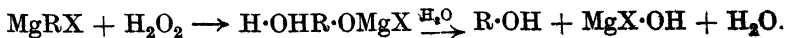
[16] E. J. Lush, Brit. Pat. 180016; *A.*, i, 625.
[17] O. Traun, Brit. Pat. 156148; *A.*, i, 522.
[18] *J. Soc. Chem. Ind.*, 1922, **41**, 303т; *A.*, i, 917.
[19] E. Müller, *Ber.*, 1921, **54**, [B], 3214; *A.*, i, 110; H. Müller, *Helv. Chim. Acta*, 1922, **5**, 627; *A.*, i, 809.
[20] B. Oddo and R. Binaghi, *Gazzetta*, 1921, **51**, ii, 343; *A.*, i, 314.

Whilst Grignard reactions involving the use of ketones and esters usually give rise to tertiary alcohols, yet the $\alpha\alpha$-disubstituted ketones and esters lead to the formation of secondary alcohols, provided that the alkyl group in the Grignard reagent has a normal chain and contains not more than four carbon atoms.[21]   Since excellent yields are claimed for the synthesis of secondary alcohols by this procedure, the method is doubtless a valuable one.

Acetylenic glycols of the general type OH·CRR′·C⦂C·CRR′·OH. may be prepared by leading acetylene, under pressure, into the sodium derivatives of ketones, the latter sodium derivatives being easily formed by the aid of sodamide.[22]   The conditions governing the formation of another unsaturated alcohol, namely, vinyl alcohol, have been studied ·by Evans and Looker, whilst a new synthesis of glycerol [23] from glycollaldehyde is effected by condensation with nitromethane, followed by reduction and treatment of the resulting aminoglycol with nitrous acid.   In a similar way, glucose has been converted into crystalline α-glucoheptol.

Of the available routes to the formation of the pure representatives of the chloro- and bromo-hydrins of glycerol, that which has been explored by J. Read and E. Hurst [24] is to be recommended.   Allyl alcohol provides a suitable starting point, and it is shown that the hypohaloginous acids combine smoothly, yielding the mono-halogenhydrins and also, as by-products, the dihalogenhydrins.

A novel and welcome variation of the usual reagents for the preparation of chlorohydrins from ethylenic hydrocarbons is provided by the recognition that monochlorocarbamide, obtained by chlorinating urea in aqueous solution, readily combines with olefines in presence of dilute acetic acid to give the corresponding chlorohydrins.[25]   Several new chlorohydrins and their related ethylene oxide compounds have been obtained by this means, and, judging from the applications which have so far been studied, the reaction seems to be general.   Ethylene oxide itself is of value in preparing by a direct method the chloroethyl esters of all types of acids.[26]   This gaseous oxide combines additively with acid chlorides at their boiling point with immediate formation of esters in which the halogen is present in the alcohol residue.   Another use to which chlorohydrins may be put is illustrated by the almost quantitative synthesis of ethylene cyanohydrin by means of sodium cyanide in cold aqueous solution.

[21] J. Leroide, *Ann. Chim.*, 1921, [ix], **16**, 354; *A.*, i, 215.

[22] R. Locquin and S. Wouseng, *Compt. rend.*, 1922, **174**, 1427; *A.*, i, 617.

[23] A. Pictet and A. Barbier, *Helv. Chim. Acta*, 1921, **4**, 924; *A.*, i, 4.

[24] *T.*, 1922, **121**, 989.

[25] A. Detœuf, *Bull. Soc. chim.*, 1922, [iv], **31**, 102, 169, 176; *A.*, i, 236.

[26] J. Altwegg and J. Landrivon, U.S. Pat. 1393191; *A.*, i, 315.

The well-known phenomenon of the occurrence of hydrogen peroxide during the atmospheric oxidation of ether is now ascertained to be due to the formation of an ether peroxide [27] which is volatile and decomposes under the influence of light, but in presence of acidified water hydrogen peroxide is produced quantitatively.

Aldehydes and Ketones.

In the foregoing section devoted to the alcohols and their derivatives, reference is made to developments in the synthetic production of formaldehyde and methyl alcohol. Numerous researches have been undertaken on problems involving the study of derivatives of formaldehyde, and some of these have an industrial application. An example is the preparation of a powerful reducing agent by suspending zinc dust in "formalin" solution and passing sulphur dioxide into the mixture through a Chamberland filter.[28] The zinc–formaldehyde hyposulphite which crystallises from solution is claimed to be more economical in use for the reduction of dyestuffs than the usual reagents. Distillation of formaldehyde in presence of sulphur dioxide gives rise to sulphiformin, $OH \cdot CH_2 \cdot O \cdot SO \cdot OH$, which has antiseptic and reducing properties and is easily decomposed into formic acid.[29] A similar transformation of formaldehyde into formic acid by the use of catalysts is described which resembles the Cannizzaro reaction.

Among the novel reactions of formaldehyde may now be included its combination with hydrogen phosphide [30] in presence of hydrochloric acid, giving a compound of the type $PCl(CH_2 \cdot OH)_4$ which is crystalline. Other combinations of phosphorus compounds with aldehydes and ketones are already known, and it is noteworthy that these are readily formed by the agency of phosphorus trihalide.

Reactions which lead to the synthesis of acetaldehyde or acetic acid from acetylene continue to be actively investigated, and minor advances in technique have been recorded during the year. Variations of catalysts or the media in which they function represent the general lines of inquiry, and a difficulty has been overcome by utilising steam for the effective removal of the acetaldehyde before it has had opportunity to form condensation complexes *in situ*. In favourable circumstances, the yield of aldehyde approaches 80 per cent. The yield of acetaldehyde in the ordinary

[27] A. M. Clover, *J. Amer. Chem. Soc.*, 1922, **44**, 1107; *A.*, i, 619.

[28] Ph. Malvezin, Ch. Rivalland, and L. Grandchamp, *Compt. rend.*, 1921, **173**, 1180; *A.*, i, 8.

[29] Ph. Malvezin, *Ind. Chimique*, 1921, **8**, 311, from *Chem. Zentr.*, 1921, iii, 1118; *A.*, i, 222.

[30] A. Hoffman, *J. Amer. Chem. Soc.*, 1921, **43**, 1684; *A.*, i, 8.

laboratory preparation [31] from alcohol is similarly enhanced by the simple device of stirring the chromate mixture in order to disengage the aldehyde rapidly from the solution.

Since the initiation of the Fernbach-Weizmann fermentation process for the production of acetone, numerous attempts have been made to devise uses for the n-butyl alcohol which is the accompanying by-product. Several claims consequently appear in the patent literature describing the conversion of this alcohol into butaldehyde and butyric acid, and doubtless similar cheap and useful reagents will be made available.

The older methods for the reduction of acid chlorides to aldehydes were superseded by the procedure introduced by Rosenmund several years ago. It is satisfactory to find that the variability in the efficiency of the nickel and palladium catalysts in his earlier work has been largely overcome and a more trustworthy procedure is available. Extension of this work by Rosenmund and his collaborators to the dialdehydes [32] is illustrated by the case of sebacicdialdehyde, $C_8H_{16}(CHO)_2$, which is obtainable in a yield of 80 per cent. by the use of hydrogen in presence of palladised kieselguhr and "sulphured" quinoline. Direct formation of acetals proceeds smoothly by careful adjustment of conditions, and it is noteworthy that ammonium chloride functions equally with hydrogen chloride as a catalyst in this connexion.[33] Neutralisation of the acid with sodium ethoxide before isolation of the product has certain advantages over the earlier practice.

Studies on keto-enolic tautomerism which owe so much to the work of Knorr and his collaborators have been amplified by the introduction of interesting examples. As was to be expected, the weapons with which earlier attacks on this problem were made are not found to be generally applicable, and neither the coloration with ferric chloride nor the bromine titration method of K. H. Meyer is useful in all cases for the diagnosis of enol forms.[34] The vagaries of enolisation are responsible for many reactions which are imperfectly understood, and it excites no surprise to learn that diacetylacetone [35] has not the usually accepted open-chain formula. Reactions of acetylacetone with tellurium and selenium tetrachlorides reveal very strikingly the residual affinity of such compounds, and the elegant researches of Morgan, Drew, and

[31] C. E. Adams and J. Williams, *J. Amer. Chem. Soc.*, 1921, **43**, 2420; *A.*, i, 222.

[32] K. W. Rosenmund, F. Zetzsche, C. Flütsch, and F. Enderlein, *Ber.*, 1921, **54**, [B], 2888; *A.*, i, 39; *ibid.*, 1922, **55**, [B], 609; *A.*, i, 431.

[33] R. D. Haworth and A. Lapworth, *T.*, 1922, **121**, 76.

[34] H. P. Kaufmann, *Ber.*, 1922, **55**, [B], 2255; *A.*, i, 985.

[35] J. N. Collie and Amy A. B. Reilly, *T.*, 1922, **121**, 1984.

Barker [36] elucidate a recondite problem. The work of J. F. Thorpe, C. K. Ingold, and their collaborators traverses the whole field of tautomeric change, and it is impossible to deal adequately with a subject of these dimensions within the confines of this Report.

Pyrogenic decomposition of acetone [37] leads almost exclusively to scission into keten and methane, and ultimately from the keten into carbon monoxide and ethylene, whilst with higher ketones both saturated and ethylenic hydrocarbons are formed by gain or loss of hydrogen by the radicles at the moment of disruption. Such data are of value in controlling the process of acetone manufacture from calcium acetate. Union of nitrosyl chloride with a normal paraffin in sunlight illustrates a novel and indirect means of oxidation, since heptane, passing through the stages of dipropylnitrosomethane and the isomeric oxime, is converted into dipropyl ketone.[38] Auto-oxidation is a phenomenon which has been investigated closely, with special reference to the inhibitory effects of many phenolic compounds.[39] Quinol, especially, suppresses the auto-oxidation of crotonaldehyde even when the " anti-oxygen " is present in so slight an amount as 1 : 100,000.

Acids and their Derivatives.

Several papers dealing with hydrocyanic acid reflect the interest which attaches to its synthesis from materials of a widely different nature, and its trimeride appears to be represented by aminodicyanomethane. The question has been reopened as to the existence of the tautomeric form, HNC, in equilibrium with the normal nitrile form and evidence of this tendency is adduced.[40] Standard reactions for the preparation of formic, oxalic, acrylic, maleic, and fumaric acids have been revised, and a convenient method of obtaining pure methyl acetate is provided by digestion of 70 per cent. acetic acid with methyl oxalate. The behaviour of acids in ultra-violet light forms the subject of several papers, the halogen acids displaying a marked capacity to decompose into paraffin halides.

Great importance attaches to the precise regulation of conditions for the α-bromination of acids. The Hell-Volhard method leads to variable results in different instances, and a new series of experi-

[36] G. T. Morgan, H. D. K. Drew, and T. V. Barker, *T.*, 1922, **121**, 922, 2432; compare W. Madelung, *Annalen*, 1922, **427**, 35; *A.*, ii, 344.

[37] (Mlle) E. Peytral, *Bull. Soc. chim.*, 1922, [iv], **31**, 122; *A.*, i, 222; A. Mailhe, *ibid.*, 863; *A.*, i, 985.

[38] E. V. Lynn and O. Hilton, *J. Amer. Chem. Soc.*, 1922, **44**, 645; *A.*, i, 417.

[39] C. Moureu and C. Dufraisse, *Compt. rend.*, 1922, **175**, 127; *A.*, i, 824.

[40] Edith H. Usherwood, *T.*, 1922, **121**, 1604.

ments [41] substantiate the theories of Aschan and others that the reaction consists essentially in the addition of bromine to an enolic form of the acid, followed by loss of hydrogen bromide, and these conditions are attained by using molecular proportions of bromine along with 2 per cent. of red phosphorus. Traces of water in the acids, or the acids themselves, serve to generate sufficient hydrogen bromide to promote enolisation, a condition which has been followed in another connexion by Lapworth. Bromination of ethyl acetoacetate under conditions resembling those of gaseous chlorination leads to the α-bromo- instead of the ω-bromo-compound.[42] The expense attending the use of ethyl β-iodopropionate as a synthetic agent is obviated by substituting in its place the esters of β-chloro- and β-bromo-propionic acids which are now obtainable from trimethylene glycol, the latter being a by-product from the glycerol fermentation of sugars.[43]

A new explanation, differing from that of Claisen, for the aceto-acetic ester synthesis is furnished by an interesting paper [44] describing the isolation of ketenacetal (II), as the result of spontaneous decomposition of the primary product in ethereal suspension, or by the action of water. It is suggested that the first product of the condensation is the compound (I), which changes as described above or is decomposed by dilute acids to give ethyl acetoacetate :

$$\text{(I.)} \quad CH_3 \cdot CO \cdot CH_2 \cdot C \underset{\underset{ONa}{\overset{OEt}{\diagdown}}}{\overset{OEt}{\diagup}} \quad \begin{array}{l} \longrightarrow CH_3 \cdot CO \cdot CH_2 \cdot CO_2Et \\[4pt] \longrightarrow CH_2 \colon C(OEt)_2 + CH_3 \cdot CO_2Na \quad \text{(II.)} \end{array}$$
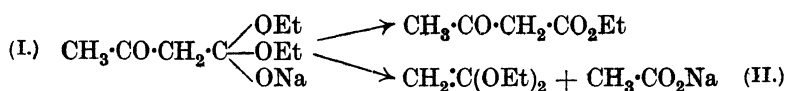
The publication of other confirmatory evidence is promised, and will be awaited with interest.

Addition of hydrogen cyanide to ethyl α-cyano-β-methyl-glutaconate and its homologues occurs readily on treatment of the esters with an aqueous alcoholic solution of potassium cyanide or with hydrogen cyanide containing sufficient of its potassium salt to ensure the presence of cyanogen ions.[45] With simple αβ-unsaturated esters such as ethyl crotonate or dimethylacrylate, the additive reaction proceeds smoothly with the formation, after hydrolysis, of substituted succinic acids,[46] and similar products may be obtained from aldehydes by a simplified procedure involving the use of potassium cyanoacetate.

[41] C. F. Ward, T., 1922, 121, 1161.

[42] L. 1. Smith, J. Amer. Chem. Soc., 1922, 44, 216; A., i, 318.

[43] C. A. Rojahn, Ber., 1921, 54, [B], 3115; A., i, 105.

[44] H. Scheibler and H. Ziegner, ibid., 1922, 55, [B], 789; A., i, 426.

[45] E. Hope and W. Sheldon, T., 1922, 121, 2223.

[46] Lucy Higginbotham and A. Lapworth, ibid., 49; A. Lapworth and J. A. McRae, ibid., 1699.

Böeseken has extended his boric acid method of investigating configuration by applying it to acids of different types. Mono-substituted α-hydroxy-acids, $OH \cdot CHR \cdot CO_2H$, show an increase in conductivity in boric acid solutions, but this increase is greater than with disubstituted acids, $OH \cdot CRR' \cdot CO_2H$, and this serves to differentiate the two types. The attainment of this result is attributed to the space relation of the hydroxyl groups. It is suggested that in aqueous solution the carboxyl group is hydrated to $-C(OH)_3$, and in concentrated solution α-keto-acids contain the residue $-C(OH)_2 \cdot C(OH)_3$. Careful perusal of the systematic summary of the results which have been accumulated up to date will be well repaid.[47]

Speculation as to the mechanism of an important group of reactions investigated by Thorpe, Ingold, and their colleagues continues to receive experimental fulfilment. Although the Reporter can do little more within the allotted space than refer the reader to the original papers, mention should be made of the discovery that the Michael condensation is a reversible reaction. The first recorded example of the Michael reaction was the condensation of ethyl sodiomalonate with ethyl cinnamate :

$$CHPh{:}CH \cdot CO_2Et + CH_2(CO_2Et)_2 \rightleftharpoons CHPh{<}^{CH(CO_2Et)_2}_{CH_2 \cdot CO_2Et}.$$
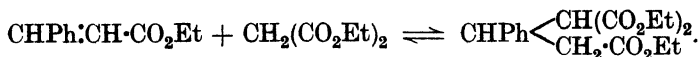
The reaction proceeds from left to right, giving a yield of 35 per cent. of the product. If, however, the product after isolation is submitted to the heating conditions which promote its formation, it is found that the reaction proceeds from right to left to the extent of 60 per cent., about 35—40 per cent. only remaining unchanged. The results furnish decisive evidence in this and other cases that a definite equilibrium is reached determining the amount of the condensation product which may be isolated from the Michael reaction.[48]   In general, the change may be represented

$$CR_2{:}CY \cdot CO_2Et + CH[H]X \cdot CO_2Et \rightleftharpoons {}^{CR_2 \cdot CY[H] \cdot CO_2Et}_{CHX \cdot CO_2Et},$$
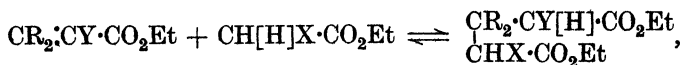
and it is suggested that this bears a striking resemblance to the three-carbon tautomerism of substituted glutaconic esters, so that the latter change may be regarded as an intramolecular Michael condensation :

$$^{CR{:}CY \cdot CO_2Et}_{C[H]X \cdot CO_2Et} \rightleftharpoons {}^{CR \cdot CY[H] \cdot CO_2Et}_{CX \cdot CO_2Et}.$$
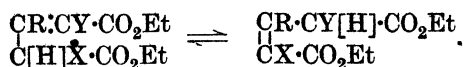
[47] L. Boeseken, *Rec. trav. chim.*, 1921, **40**, 553; *A.*, 1921, i, 843.
    [48] C. K. Ingold and Powell, *T.*, 1921, **119**, 1976; C. K. Ingold, E. A. Perren, and J. F. Thorpe, *ibid.*, 1922, **121**, 1765.

A series of researches on the synthesis of the polyacetic acids of methane has reached completion and has resulted in the isolation of all the four compounds,

(I.) $CH(CH_2 \cdot CO_2H)_3$ (II.) $CO_2H \cdot C(CH_2 \cdot CO_2H)_3$

(III.) $(CO_2H \cdot CH_2)_2C:CH \cdot CO_2H$ (IV.) $C(CH_2 \cdot CO_2H)_4$,
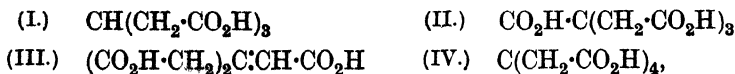
which may empirically be considered as derivable from glutaconic acid.[49]

The isomerism of the glutaconic acids and their derivatives is represented by an ever-growing literature, and the elucidation of this subject owes much to the work of Thorpe and Ingold. Feist and his co-workers have failed to obtain the *cis-* and normal forms of β-phenyl-α-methylglutaconic acid described by Thorpe and Wood in 1913, but have confirmed the isolation of the *trans*-form and also of a new isomeride which is described as the true *cis*-modification. Feist's general conclusions [50] favour the view that the glutaconic acid series conforms to the ordinary type of geometric isomerism represented by maleinoid and fumaroid forms, and that any apparent variation is one of degree and not of principle.

An interesting study of the formation and properties of β-lactones suggests the speculation that these compounds occur more commonly than is usually supposed.[51] Since the hydrolysis of β-lactones is not a reversible change, they are conveniently derived from β-halogenated acids by hydrolysis in neutral solution.

A large number of papers deal with the relationships of the complex fatty acids, and the following facts emerge. The so-called rapic acid is identical with oleic acid. A new acid isolated from peat by Aschan and named humoceric acid is not identical with lignoceric acid from beechwood tar, since the latter is now shown to be tetracosoic acid. It is obtained on oxidising cerebronic acid, which is itself an α-hydroxypentacosoic acid and does not contain a normal chain. Holde and his co-workers have isolated pure erucic acid, and the anhydrides of both this and brassidic acid and also those of the fatty acids of linseed oil have been prepared. The positions of the double linkings in linoleic acid are allocated by a study of sativic acid (tetrahydroxystearic) involving progressive elimination of the hydroxyl groups, and the constitution of sativic acid is determined by alkali fusion. Caution, however, should be observed in view of the instances of a benzylic acid transformation which are known to occur under this treatment.

[49] C. K. Ingold and L. C. Nickolls, *T.*, 1922, **121**, 1638.

[50] F. Feist, *Annalen*, 1922, **428**, 25, 59, 69; *A.*, i, 521.

[51] H. Johansson and S. H. Hagman, *Ber.*, 1922, **55**, [*B*], 647; *A.*, i, 425.

Electrosynthesis of azelaic and thapsic acid [52] has been achieved, and it is now clear that the latter is identical with *n*-tetradecane-dicarboxylic acid.

Halogen Compounds.

A greatly increased yield of methyl bromide is obtainable by a modified procedure [53] which eliminates the usual risk of the production of flame. The usual mixture of methyl alcohol and red phosphorus should preferably be boiled for fifteen minutes before the addition of bromine to the gently boiling liquid. When bromine is mixed with methylal in a freezing mixture, the chief products are methyl bromide and dibromomethylal, $CBr_2(OMe)_2$. The latter is an effective methylating agent, readily converting aniline into methylaniline, sodium cinnamate into the methyl ester, β-naphthol into the ether, and sodiomalonic ester into the substitution derivative.[54] A convenient preparation of vinyl halides *in situ* is rendered possible by distilling concentrated halogen acids in presence of calcium carbide while simultaneously saturating the mixture with the gaseous hydrogen halide. Certain metallic chlorides act as accelerators, but ferric chloride promotes the formation of dichloroacetaldehyde.[55] Chloroacetyl chloride has been obtained by the catalytic oxidation of chlorinated ethylene, and this reagent has been applied with success in the preparation of cellulose esters.[56] Various catalytic processes leading to the polychloroethanes from acetylene have been described. Arsenic trichloride combines additively with acetylene to give the primary, secondary, and tertiary β-chlorovinylarsines, which readily undergo oxidation to the corresponding derivatives of arsenic acid. Such compounds are reminiscent of the reactions which lead to the formation of ββ′-dichlorodiethyl sulphide, and it is satisfactory to observe that the same authors [57] have resolved many doubts as to the nature of the reaction between ethylene and the sulphur chlorides and have revealed the identity of the related products isolated by other workers. Hydrolysis of "mustard gas" with alcoholic potassium hydroxide [58] gives rise to divinyl sulphide, which again forms a dichloride with hydrochloric acid, but this product is the αα-dichloro-compound and is a non-vesicant, as

[52] Mabel Carmichael, *T.*, 1922, **121**, 2545.

[53] W. Steinkopf and G. Schwen, *J. pr. Chem.*, 1921, [ii], **102**, 363; *A.*, 1921, i, 841.

[54] F. Feist, *Z. angew. Chem.*, 1922, **35**, 489; *A.*, i, 912.

[55] Brit. Pat. 156120; *A.*, i, 517.

[56] W. L. Barnett, *J. Soc. Chem. Ind.*, 1921, **40**, 286; *A.*, i, 232; and D.R.-P. 340872.

[57] F. G. Mann and Sir W. J. Pope, *T.*, 1922, **121**, 1754, 594.

[58] S. H. Bales and S. A. Nickelson, *ibid.*, 2137.

indeed is the oxygen analogue of mustard gas, the isolation of which is recorded.

Robinson's theory of the induced polarity of atoms has stimulated inquiry as to the labile character of certain groups in a selected series of compounds. In several papers, A. K. Macbeth and his collaborators [59] have studied this problem in great detail, and their general method of investigation is to submit selected halogen compounds, among others, to the action of a definite range of reducing agents and measure by volumetric methods the nature and extent of the reducing action. Certain halides readily lose their halogen atoms under these conditions, and their labile character is attributed to the development of positive polarity by reason of the position such atoms occupy in relation to other groups. The suggestion that bromomalonic esters owe the labile nature of the halogen to the presence of an oxygen-halogen linking appears to be at variance with the results obtained by a comparison of the absorption spectra of such compounds with those of ethyl malonate. The results recorded find a reasonable explanation in the theory which the authors have adopted.

On the other hand, Gupta and Thorpe [60] find this explanation unacceptable in the cases which they have examined and prefer the tautomeric hypothesis which correlates the labile character of halogen atoms in selected carbon compounds with the tendency of the latter to acquire a hydrogen atom so located as to promote enolisation, and their theory is supported by other workers.

Optical Activity.

An almost unique case of the optical activation of a racemic compound is afforded by the observation that on mixing *l*-malic acid with solutions of the alkali salts of racemic acid *d*-tartaric acid is liberated.[61] A parallel example is furnished by *dl*-phenyl-methylcarbinol, which undergoes catalytic dehydration in the presence of 1 per cent. of camphorsulphonic acid at 100° with the formation of the lævorotatory ether oxide, whilst the unchanged carbinol was also activated.[62] Rather different in principle is the procedure adopted for the activation or partial resolution of *dl*-mandelic acid. The *l*-menthyl ester on chlorination with thionyl chloride, followed by hydrolysis, gives rise to *l*-phenylchloroacetic acid.[63] The practice of separating optical isomerides by fractional

[59] T. Henderson and A. K. Macbeth, *T.*, 1922, **121**, 892; E. L. Hirst and A. K. Macbeth, *ibid.*, 904; H. Graham and A. K. Macbeth, *ibid.*, 1109.

[60] B. M. Gupta and J. F. Thorpe, *ibid.*, 1896.

[61] A. McKenzie and Nellie Walker, *ibid.*, 349.

[62] H. Wuyts, *Bull. Soc. chim. Belg.*, 1921, **30**, 30; *A.*, 1921, i, 506.

[63] A. Shimomura and J. B. Cohen, *T.*, 1921, **119**, 1818.

crystallisation of their salts was illustrated in the case of lactic acid by Purdie. An extension of this procedure to organic esters has demonstrated that *l*-menthyl esters of atrolactinic acid and α-hydroxy-β-phenylpropionic acid are resolvable by crystallisation from solvents,[64] since on hydrolysis of the crystals the active acids are isolated. The usual practice for the resolution of racemic compounds is generally regarded as too difficult an exercise to be handled by a student as a laboratory preparation, but the simplified manipulation described by Kenner in the case of methyl-*n*-hexyl-carbinol incidentally overcomes this objection,[65] and provides an easy access to a useful optically active alcohol.

Synthesis of optically active compounds by methods which involve activation simultaneously with the creation of the system of groupings responsible for asymmetry is the only genuine kind of asymmetric synthesis. The following recent examples [66] appear to come within this category : the cyanohydrin synthesis applied to *iso*valeraldehyde and *p*-tolualdehyde in presence of emulsin gives rise to dextrorotatory nitriles; yeast fermentation in presence of pyruvic acid or of acetylcarbinol leads to optically active acetylmethyl-carbinol or *l*-propylglycol, respectively.

The discovery of Franchimont that ethyl tartrate is a crystalline solid with a freezing point of $18\cdot7°$ has contributed a new criterion of purity, and the admirable investigations [67] based on material conforming to this new standard have resulted in a series of re-determinations of specific rotation, density, refractive index, and dispersion, using light of representative wave-lengths. The observed specific rotations range from $+ 6\cdot87°$ in the green to $- 12\cdot2°$ for the last photographic reading in the ultra-violet and include thirty-four values for the intermediate lines of the spectrum. The rotatory dispersion is in close agreement with that calculated by using two terms of the Drude equation. Comparative measurements of the interfacial tension between aqueous solutions of the two active tartaric acids and racemic acid in contact with inert liquids reveal no differences for the *d*- and *l*-forms, but a marked divergence from this value for racemic acid, and this is adduced as evidence of the existence in solution of the racemic acid molecule. On increasing the dilution, there is a clear indication of dissociation into *d*- and *l*-forms. It is demonstrated that the type of union found in racemic acid is not restricted to the two antipodes, since a like combination may be artificially produced between

[64] H. Wren and E. Wright, *T.*, 1921, **119**, 798.

[65] *T.*, 1922, **121**, 2540.

[66] L. Rosenthaler, *Fermentforsch.*, 1922, **5**, 334; *A.*, i, 480; J. Hirsch, *Biochem. Z.*, 1922, **131**, 178; *A.*, i, 973. Compare *A.*, 1921, i, 150.

[67] T. M. Lowry and J. O. Cutter, *T.*, 1922, **121**, 532.

d- and *i*-tartaric acid, the complex containing one molecule of each acid along with water of crystallisation as in racemic acid, the rotatory power being thereby halved.[68]

Evidence is available which disposes of the assumption that racemisation of *l*-mandelamide with alkali is to be attributed to enolisation. An explanation which is supported by experiment [69] is that alkali or potassium ethoxide combines additively with the amide as in the Claisen reactions, subsequent loss of water or alcohol producing an inactive compound. The changes may be expressed :

$$\underset{\text{lævo.}}{\overset{\displaystyle \text{Ph·CH·OH}}{\underset{\displaystyle \text{NH}_2\text{·C:O}}{|}}} \rightarrow \underset{\text{lævo.}}{\overset{\displaystyle \text{Ph·CH·OH}}{\underset{\displaystyle \text{NH}_2\text{·C}\!<^{\text{OEt}}_{\text{OK}}}{|}}} \rightarrow \underset{\text{inactive.}}{\overset{\displaystyle \text{Ph·C·OH}}{\underset{\displaystyle \text{NH}_2\text{·C·OK}}{||}}} \rightarrow \underset{\text{racemic.}}{\overset{\displaystyle \text{Ph·CH·OH}}{\underset{\displaystyle \text{NH}_2\text{·C:O}}{|}}}$$
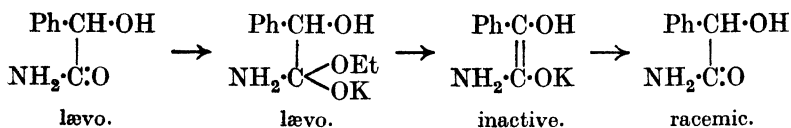
The racemisation of the mandelonitrile residue in amygdalin is explicable on a similar principle. The presence of a migrational hydrogen atom on the asymmetric carbon atom appears to lead in all such cases to racemisation; this tendency is suppressed by substitution of a methyl group for the hydrogen atom or alternatively by replacing the phenyl residue by benzyl. On the other hand, the tendency is increased by the presence of a methoxyl or tolyl group in place of the hydroxyl group attached to the asymmetric carbon atom.

Of the many examples of resolution into optically active forms which have been communicated during the period under review, one of the most interesting [70] is that of the keto-dilactone of benzophenone-2 : 4 : 2 ′ : 4′-tetracarboxylic acid shown below :
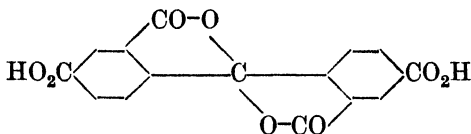
The compound affords another example of the existence of optical enantiomorphs containing no asymmetric atom. Theoretically, the molecule is divisible at the central spirane carbon atom into two identical halves, but the molecular asymmetry is attributable to the fact that these two halves lie in different planes which meet and intersect at right angles at this central atom. The resolution has been achieved by the use of *l*-α-phenylethylamine. Taking

[68] Ph. Landrieu, *Bull Soc. chim.*, 1922, **33**, 667; *A.*, i, 808; S. W. Penny-cuick, *J. Amer. Chem. Soc.*, 1922, **44**, 1133; *A.*, i, 624.

[69] A. McKenzie and Isobel A. Smith, *T.*, 1922, **121**, 1348.

[70] W. H. Mills and C. R. Nodder, *ibid.*, 1921, **119**, 2094.

advantage of the existence of $\alpha\alpha'$-dibromoadipic acids in both *meso-* and *racemic* forms, W. H. Perkin and E. Robinson [71] have condensed the esters of these acids with ethyl malonate in order to synthesise the geometric isomerides of *cyclo*pentane-1 : 2 : 3-tricarboxylic acid :

$$\begin{array}{l} CH_2\text{---}CH\cdot CO_2H \\ \qquad\quad CH\cdot CO_2H \\ CH_2\text{---}CH\cdot CO_2H \end{array}.$$
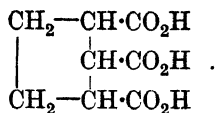
Two of these isomerides, the *cis-trans-cis*, and the *cis-cis-cis*, are *meso*-forms and a third, the *cis-trans-trans*, is a *racemic* form, which was resolved by means of brucine.

Carbohydrates.

Monosaccharides.—Improved methods for the preparation of a number of sugars and their derivatives are reported in the literature of the year, among which are included fructose, mannose, galactose, raffinose, sorbitol, inulin, and gluconic acid. Scrutiny of the procedure involved in the oxidation of hexoses has revealed an unexpected result. At the ordinary temperature and in the absence of air, nitric acid transforms glucose or gluconic acid into α-keto-gluconic acid, in the formation of which the oxidation of a secondary alcohol group is involved.[72] Fischer's degradation of d-saccharic acid by oxidation with permanganate into d-tartaric acid proved the configuration of the groups attached to the second and third carbon atoms of the glucose chain. The diamide of d-saccharic acid yields, however, l-tartaric acid through the related dialdehyde on treatment with bromine and potassium hydroxide,[73] and this proves the configuration of the groups attached to carbon atoms 3 and 4.

$$\begin{array}{lll}
\begin{array}{l}
CO_2H \\
H\cdot C\cdot OH \\
HO\cdot C\cdot H \\
CO_2H
\end{array}
\xleftarrow[]{\ KMnO_4\ }
\begin{array}{l}
CO_2H \\
H\cdot C\cdot OH \\
HO\cdot C\cdot H \\
H\cdot C\cdot OH \\
H\cdot C\cdot OH \\
CO_2H
\end{array}
\xrightarrow[\text{on amide}]{\ KOH\ and\ Br_2\ }
\begin{array}{l}
CO_2H \\
HO\cdot C\cdot H \\
H\cdot C\cdot OH \\
CO_2H
\end{array}
\end{array}$$
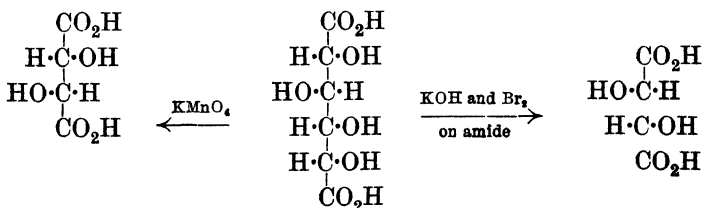
Collateral evidence bearing on the character of the oxide linking in simple hexoses is furnished by the synthesis of γ- and δ-hydroxy-

[71] *T.*, 1921, **119**, 1392.

[72] H. Kiliani, *Ber.*, 1922, **55**, [*B*], 75, 493; *A.*, i, 223, 321.

[73] M. Bergmann, *ibid.*, 1921, **54**, [*B*], 2651; *A.*, i, 7.

aldehydes and ketones.[74] The location of the hydroxyl group with reference to the aldo- or keto-group resembles that of a sugar, and it is significant that these compounds simulate the reactions of sugars. They form " glucosides " or semi-acetals with methyl-alcoholic hydrogen chloride, instead of the usual acetals, and the ease of hydrolysis of these methyl derivatives is comparable with that of the glucosides. Moreover, the typical aldehyde reactions, although not altogether suppressed, are modified or retarded by reason of the existence of the aldehydes or ketones in their more stable butylene- or amylene-oxidic forms :

$$
\begin{array}{ccc}
& & CH_3 \\
\left[\begin{array}{l} CH \cdot OH \\ CH_2 \\ O \quad CH_2 \\ CR_2 \end{array}\right. & \left[\begin{array}{l} CH \cdot OH \\ CH_2 \\ O \quad CH_2 \\ CH_2 \\ CHMe \end{array}\right. & \left[\begin{array}{l} C \cdot OH \\ CH_2 \\ O \quad CH_2 \\ CH_2 \\ CH_2 \end{array}\right. \\
\text{(I.)} & \text{(II.)} & \text{(III.)} \\
\text{(γ-hydroxy-aldehyde).} & \text{(δ-hydroxy-aldehyde).} & \text{(δ-acetylbutylalcohol).}
\end{array}
$$

Cyclic forms of :
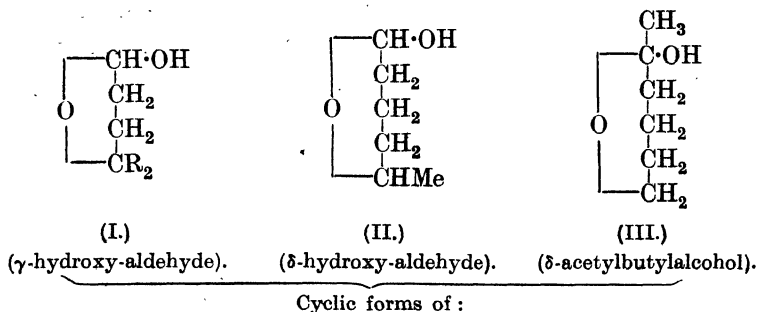
The methyl semi-acetal of III contains an amylene oxide ring and the sensitiveness of this analogue of methylfructoside towards extremely dilute acids is reminiscent of the behaviour of the γ-glucosides or fructosides. Should the amylene-oxidic structure be assigned to the γ-sugars, this characteristic property will receive sufficient explanation from the analogy which has been drawn.

A re-investigation of the acetone derivatives of glucose indicates that their structure conforms to the γ-glucose type, and formulæ are ascribed to those compounds which represent γ-glucose by a propylene-oxidic structure. On the other hand, both fructose mono- and di-acetones are derivatives of ordinary lævorotatory or butylene-oxidic fructose, and it is remarkable that the same compounds are formed either from ordinary fructose or γ-methyl-fructoside.[75]

The chemistry of glucosamine has been advanced by the recognition and study of the new β-form, and a comparison of its molecular rotation with that of the α-form shows that these values are in agreement with Hudson's rule if glucosamine is accepted as 2-aminoglucose, and at variance with its relationship to mannose.

[74] B. Helferich and M. Gehrke, *Ber.*, 1921, **54**, [*B*], 2640; *A.*, i, 9; B. Helferich and T. Malkomes, *ibid.*, 1922, **55**, [*B*], 702; *A.*, i, 431; M. Bergmann and A. Miekeley, *ibid.*, 1390; *A.*, i, 618.

[75] J. C. Irvine and J. Patterson, *T.*, 1922, **121**, 2146.

Since glucosamine has been converted into both glucose and man-nose, the latter change must involve a Walden inversion. Con-densation of triacetyl bromoglucosamine with salicylaldehyde does not occur through the phenolic group of the latter to give a gluco-side, but involves a union of the aldehyde residue of salicylaldehyde with the amino-group of the sugar. The bromine atom in the reducing position in the sugar derivative thus remains intact, and is removed by solution in alcohols and leads to glucoside formation. The latter reaction is accompanied by a gradual change of rotation which, in the absence of precise knowledge of the structure of the salicylidene derivative, was formerly described as pseudo-muta-rotation. Whilst serving to elucidate an apparent anomaly in the optical behaviour of a supposed glucoside, this research [76] furnishes additional evidence of the tendency of glucosamine to form deriv-atives of the betaine-ring type. Thus, whilst triacetyl methyl-glucosamine combines to give an 80 per cent. yield of the salicylidene derivative and presumably exists largely as an amino-hexose complex, the de-acetylated methylglucosamine yields only 26 per cent. of the salicylidene product, the inference being that free methylglucosamine exists mainly in the betaine form in which the glucosidic methyl group is united with nitrogen, giving the

cyclic complex : $\begin{array}{c}-\mathrm{CH-O}\diagup\mathrm{Me}\\ |\qquad\quad|\diagdown\\ \mathrm{CH-N}\diagup\mathrm{H}\\ |\qquad\diagdown\mathrm{H}\end{array}$. The capacity of glucosamine to

condense with reagents varied in type is also illustrated by its transformation into crystalline heterocyclic compounds of the glyoxaline and pyrrole class in presence of potassium thiocyanate or silver cyanate,[77] reactions which bear a resemblance to the first stage in Pyman's synthesis of histidine. The idea that glucose, reacting as an aldehyde, gives a glucose–ammonia which is an analogue of aldehyde–ammonia is revived,[78] but, on the other hand, it is confirmed that glucose-anilide has the butylene-oxidic structure and is therefore aniline-glucoside.[79]

Glucosides and Disaccharides.—The recognition of the sugar residue in amygdalin has long been a subject of dispute and Fischer's tentative suggestion that the biose may be identical with maltose has often been misconstrued. The methylation of amygdalin has been accomplished by means of methyl sulphate and sodium hydroxide, giving the completely methylated amygdalinic ester.[80]

[76] J. C. Irvine and J. C. Earl, *T.*, 1922, 121, 2370, 2376.
[77] H. Pauly and E. Ludwig, *Z. physiol. Chem.*, 1922, 121, 170; *A.*, i, 953.
[78] A. R. Ling and D. R. Nanji, *T.*, 1922, 121, 1682; *J. Soc. Chem. Ind.*, 1922, 41, 151T; *A.*, i, 631.
[79] T. Sabalitschka, *Ber. deut. Pharm. Ges.*, 1921, 31, 439; *A.*, i, 247.
[80] W. N. Haworth and Grace C. Leitch, *T.*, 1922, 121, 1921.

Hydrolysis of this compound led to the isolation of butylene-oxidic forms of $2:3:5$-trimethyl glucose and $2:3:5:6$-tetramethyl glucose, from which it follows that the amygdalin-biose has the same structural formula as maltose :

$$\overset{\displaystyle \Gamma\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-O\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\urcorner}{\text{OH·CH}_2\text{·CH(OH)·CH·CH(OH)·CH(OH)·CH}}$$

$$\overset{>O}{\underset{\underset{\displaystyle L\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-O\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\urcorner}{\text{CH(OH)·CH(OH)·CH(OH)·CH·CH(OH)·CH}_2}}{}}$$
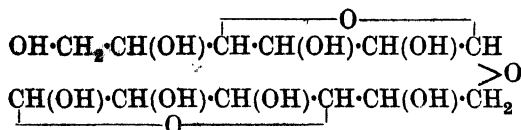
The stereochemical formula is, however, probably different from that of maltose, and the biose is most likely a glucose-β-glucoside of the above structure, and may prove to be identical with *iso*-maltose or gentiobiose.

Progress has been made in several researches on the constitution of digitonin, which is shown to contain both hexose and pentose residues. The difficult problem of the constitution of the saponins, whilst continuing to engage the attention of chemists, requires exceptional patience and resource, and it would seem that greater success can only be attained by an extended study of the crystalline sapogenins, which are related to the terpenes.[81] The glucose residue in indican appears to be of the normal butylene-oxide type.[82]

A biochemical synthesis of α-methylmannoside is reported [83] and also the synthesis of new condensation complexes from helicin.

Polysaccharides.—A significant feature of the work of the year is the unprecedented volume of researches on the constitution of the polysaccharides. It is only possible to reflect the general trend of the published results, which are often so contradictory that little finality is to be expected at the present stage. Starch, when degraded by bacteria, gives rise to a series of products, many of them crystalline, which are represented by a formula $(C_6H_{10}O_5)_n$, where n is a small integer such as 2, 3, 4, 6, 8, and these compounds are known as the di-, tri-, tetra- (etc.) amyloses. In relation to starch itself, these are comparatively simple substances, and their investigation may obviously be expected to throw some light on the structure of starch. On distilling potato-starch in glycerol, a new depolymerised product is isolated, differing from the above triamylose, but isomeric with it, and this is named trihexosan.[84]

[81] A. Windaus and K. Weil, *Z. physiol. Chem.*, 1922, **121**, 62; *A.*, i, 848; A. W. van der Haar, *Rec. trav. chim.*, 1921, **40**, 542; *A.*, 1921, i, 877.

[82] A. K. Macbeth and J. Pryde, *T.*, 1922, **121**, 1660.

[83] H. Hérissey, *Compt. rend.*, 1921, **173**, 1406; *A.*, i, 112; R. de Fazi, *Gazzetta*, 1922, **52**, i, 429; *A.*, i, 755.

[84] A. Pictet and R. Jahn, *Helv. Chim. Acta*, 1922, **5**, 640; *A.*, i, 987.

Pringsheim, Karrer, and others have resorted to the use of a com-
bination of the Purdie reaction and the methyl sulphate method
of methylation in a detailed study of these depolymerised starches
and, coupled with the application of acetylating agents, have
endeavoured to trace the simplest depolymerised unit of which
the starch molecule is composed. This is variously regarded as
$(C_6H_{10}O_5)_2$ or $(C_6H_{10}O_5)_3$. A. Pictet has abandoned his opinion
that starch is polymerised β-glucosan, and, along with Pringsheim,
regards $(C_6H_{10}O_5)_3$ as the unit of starch. Karrer, on the contrary,
considers that the unit is a diamylose, namely, anhydromaltose,[85]
since all methods of degrading starch had hitherto led to maltose
or polymeric forms of its anhydride. Methylation of purified rice-
starch with methyl sulphate yields a product which is incompletely
methylated and on hydrolysis gives rise to two parts of dimethyl
glucose and one part of 2 : 3 : 6-trimethyl glucose, a result which
suggests the view that the starch unit is a trihexosan, and that
the partly methylated starch (OMe = 37 per cent.) contains in
each unit a trimethyl hexose residue and two dimethyl hexose
residues. A structural formula [86] is based upon these results :

$$
\begin{array}{l}
\overline{}\text{—CH——O——CH}_2\text{·CH(OH)·CH·[CH·OH]}_2\text{·CH} \\
\text{O [CH·OH]}_2 \qquad\qquad\qquad\qquad\qquad\quad \text{O} \\
\underline{}\text{—CH} \\
\quad\ \text{CH——O——CH·[CH·OH]}_2\text{·CH·CH(OH)·CH}_2 \\
\quad\ \text{CH}_2\text{·OH}
\end{array}
$$
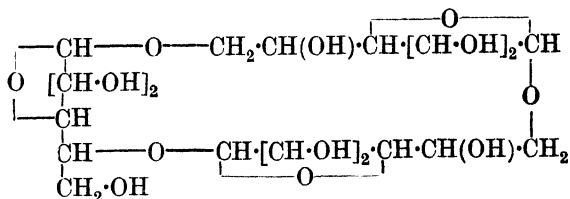
This formula takes into account the constitution already assigned
to maltose,[87] and it is noteworthy that Karrer's anhydromaltose
formula does not admit of the formation of the 2 : 3 : 6-trimethyl
glucose which has been isolated as above. It is pointed out that
ordinary starch contains nitrogen and phosphorus in chemical
combination, and an ingenious suggestion is advanced [88] that the
resistance of part of the starch grain to the action of hot water or
acids is due to the presence of condensed complexes of the starch
unit with silicic or phosphoric acid or water, the breakdown of
which gives rise to the polyamyloses.

In confirmation of earlier work, it is now established that cotton
cellulose at least contains only glucose residues.[89] A new di-

[85] P. Karrer and Elizabeth Bürklin, *Helv. Chim. Acta*, 1922, 5, 181; *A.*,
i, 435.
[86] J. C. Irvine and J. Macdonald, *Brit. Assoc. Reports*, 1922.
[87] W. N. Haworth and Grace C. Leitch, *T.*, 1919, 115, 809.
[88] G. Malfitano and M. Catoire, *Compt. rend.*, 1922, 174, 1128; *A.*, i, 527.
[89] J. C. Irvine and E. L. Hirst, *T.*, 1922, 121, 1585.

saccharide, celloisobiose, has been isolated by Ost and Knoth [90] from the products of acetolysis of cellulose. Its physical constants and the solubilities of its octa-acetate differentiate it from cellobiose, and its osazone melts at 165—167°. Although hydrolysable with greater difficulty than cellobiose, its acetate changes into a derivative of the latter sugar. A new degradation of cellulose into a biose-anhydride is reported by Hess,[91] and its tetraethyl derivative may be obtained by acetolysis of ethylated cellulose. Karrer [92] has advanced a cellulose constitution which represents the molecule as composed of two units only of anhydro-cellobiose. It was indicated two years ago by W. S. Denham [93] that methylation of cellulose could be carried to the stage at which three methoxyl groups were introduced into each $C_6H_{10}O_5$ residue, the methoxyl content being 44·6 per cent. as compared with a theoretical value of 45·6. The later work [94] describes the hydrolysis of methylated cotton cellulose containing OMe = 43·0 per cent., which gave almost entirely the 2 : 3 : 6-trimethyl glucose, thus affording a proof that the glucose residues in α-cellulose are identical in structure. The above trimethyl glucose has recently been the subject of further study [95] and the structure assigned to it by other workers is confirmed. A formula for the cellulose unit which is based upon these striking results must take into account the yield of cellobiose which is obtainable when cellulose is subjected to acetolysis, and Irvine, Denham, and Hirst suggest among others the following, which for several reasons is preferred :

$$
\begin{array}{l}
\text{CH}_2\text{·OH} \text{--------O--------} \\
\text{--CH--O--CH--------CH·[CH·OH]}_2\text{·CH} \\
\text{O [CH·OH]}_2 | \\
\text{--CH} \text{O} \\
\text{CH--------O--------CH·[CH·OH]}_2\text{·CH·CH·CH}_2\text{·OH} \\
\text{CH}_2\text{·OH} \text{--------O--------}
\end{array}
$$
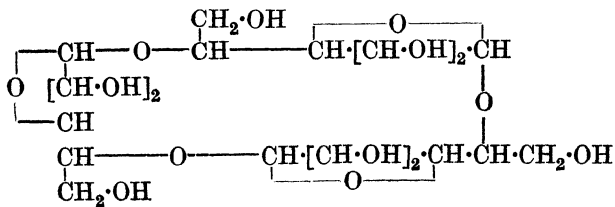
The interesting observation is made that percolation of salt solutions through cellulose produces an acid filtrate, which suggests the hydrolysis of, in one case, sodium chloride to hydrochloric acid. Aqueous washings from the cellulose so treated give an alkaline solution of alkali content almost equivalent to the acidity

[90] *Cellulosechemie*, 1922, **3**, 25; *A.*, i, 526.

[91] K. Hess and W. Wittelsbach, *Ber.*, 1921, **54**, [B], 3232; *A.*, i, 116; K. Hess, *ibid.*, 2867; *A.*, i, 12.

[92] P. Karrer, *Cellulosechemie*, 1921, **2**, 125; *A.*, i, 231.

[93] W. S. Denham, *T.*, 1921, **119**, 77.

[94] J. C. Irvine, W. S. Denham, and E. L. Hirst, *Brit. Assoc. Reports*, 1922.

[95] J. C. Irvine and E. L. Hirst, *T.*, 1922, **121**, 1213.

of the salt solution. The resultant effect on the cellulose is a matter of considerable importance.[96]

One of the many disconcerting factors encountered in the elucidation of the constitution of polysaccharides is the phenomenon of polymerisation and depolymerisation which may appear at any stage of the work. This circumstance is responsible for the isolation of no fewer than three types of trimethyl inulin, two of which are soluble in ether and show rotations of opposite sign, whilst the third is insoluble in ether. Such apparent anomalies are responsible for the frequent claims and counterclaims of different workers. Genuine progress has, however, been made in that it is finally established [97] that inulin is composed entirely of γ-fructose residues; these may conceivably be arranged in groups of three in the unit formula of the inulin molecule on the analogy of starch and cellulose, namely : $[(C_6H_{10}O_5)_3]_x$.

Nitrogen Compounds.

An inquiry [98] which will be welcomed by all chemists has been initiated with promising results into the mechanism of the synthesis of nitrogenous products in the plant. There is an experimental basis for the belief that the production of activated formaldehyde (I) from carbon dioxide under the influence of light leads, in the presence of nitrites or nitrates, to the synthesis of formhydroxamic acid (II), the photosynthetic formation of which was established by Baudisch,

$$H\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot OH + O\colon\!N\cdot OK \longrightarrow \overset{H\cdot C\cdot OH}{\underset{O\colon\!N\cdot OK}{\vphantom{X}}} \longrightarrow \overset{H\cdot C\cdot OH}{\underset{N\cdot OH}{\vphantom{X}}} + O$$

(I.)   (II.)
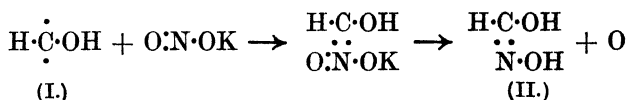
and that this product enters with remarkable ease into combination with more activated formaldehyde, giving rise to amino-acids and possibly proteins and alkaloids. The progress of this work will be watched with special interest and with the expectancy that sufficient of the laboratory products may be made available for definite characterisation and analysis. Significance is attached to the observation that sustained efforts are in progress to obtain synthetic carbamide on a considerable scale. Scrutiny of the patent literature reveals a noteworthy attempt to replace the laboratory methods by a direct commercial process which will

[96] Helen Masters, T., 1922, 121, 2026; A. Tingle, J. Ind. Eng. Chem., 1922, 14, 198; A., i; 434; E. Knoevenagel and H. Busch, Cellulosechemie, 1922, 3, 42; J. Huebner and F. Kaye, J. Soc. Chem. Ind., 1922, 41, 94T; A., i, 435.

[97] J. C. Irvine, Ettie S. Steele, and Mary I. Shannon, T., 1922, 121, 1060.

[98] E .C. C. Baly, I. M. Heilbron, and D. P. Hudson, ibid., 1078.

involve the utilisation of carbon dioxide and ammonia or of cyanamide.

The synthetic utility of cyanamide and dicyanodiamide is emphasised by the numerous examples on record of preparations of guanidine derivatives. The alkylated guanidines are readily available by the interaction of hydrochlorides of alkylamines and dicyanodiamide.[99] The latter reagent combines with ammonium perchlorate to give the explosive guanidonium perchlorate, which provides a convenient source for the preparation of guanidine and its salts.[1] Condensation of ethylene chlorohydrin with cyanamide yields the cyanoamidoethyl alcohol, whence, reacting in the form $NC \cdot NH \cdot CH_2 \cdot CH_2 \cdot OH$, guanidoethyl alcohol may be derived by combination with alcoholic ammonia. Although orthocarbonic acid and its amino-analogue have only a hypothetical existence, yet it is interesting to consider a scheme of derivation[2] which proceeds from the formula $C(NH_2)_4$ by progressive loss of ammonia from one or more molecules to guanidine, diguanidine, cyanamide; and from a polymeride of the latter, namely, melamine, $(H_2CN_2)_3$, to melam, melem, melon, and hydromelonic acid. A new member of the series, dicyanamide, $(CN)_2NH$, is an acid which is comparable in strength with hydrochloric acid.

The synthesis of *s*-aminohydroxysuccinic acid has on several occasions been prematurely reported, but success has now been achieved by heating chloromalic acid under pressure with aqueous ammonia.[3] The acid so attained is a mixture of two crystalline isomerides, which give rise on treatment with nitrous acid to racemic and *meso*tartaric acids. Applications of the aminoethanols which are of service as intermediate products in the synthesis of local anæsthetics, continue to excite interest. Although it is not possible to give an outline of the many synthetic compounds the preparation of which is chiefly described in patents, yet certain novel modes of formation may be summarised. Condensation of α-bromopropionic acid with dimethylamine and subsequent esterification lead to ethyl α-dimethylaminopropionate. Reduction of the ester group is effected by sodium in alcohol, and the product is *N*-dimethylalaninol, $Me_2N \cdot CHMe \cdot CH_2 \cdot OH$, which readily gives with methyl iodide alanine-choline iodide. The method finds application in a number of cases quoted by Karrer and his pupils.[4] Re-

[99] E. A. Werner and J. Bell, *T.*, 1922, **121**, 1790; T. L. Davis, *J. Amer. Chem. Soc.*, 1921, **43**, 2230; *A.*, i, 118.

[1] W. Marckwald and F. Struwe, *Ber.*, 1922, **55**, [B], 457; *A.*, i, 328; E. Fromm and E. Honold, *ibid.*, 902; *A.*, i, 529.

[2] E. C. Franklin, *J. Amer. Chem. Soc.*, 1922, **44**, 486; *A.*, i, 440.

[3] H. D. Dakin, *J. Biol. Chem.*, 1921, **48**, 273; *A.*, i, 143.

[4] *Helv. Chim. Acta*, 1922, **5**, 469; *A.*, i, 813.

placement of the hydroxyl group in diethylaminoethanol by halogen and condensation of this halide with sodio-malonic and -acetoacetic esters represents another line of inquiry which is in progress, whilst the use of Gabriel's phthalimide method in conjunction with the halogenohydrins provides another mode of preparation of amino-alcohols.

Prolonged heating of mercury fulminate at 90° effects an important change without alteration of the crystalline form and gives a non-explosive product which has been named pyrofulmin, but indications point to its not being a homogeneous [5] compound.

In two theoretical papers which merit attention, Staudinger [6] reviews the reactions of ketens and aliphatic diazo-compounds and reaches conclusions which suggest a modification of the constitution of the latter in accordance with the views of Thiele and Angeli.

Compounds of the type $R_2C:N:N$ are termed azenes on the analogy of the ketens, and two reactive points are indicated :

$$R_2C:N:N< \quad \text{and} \quad R_2C:N:N.$$
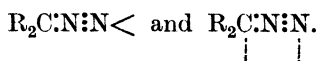
Reactions occurring at the terminal position, involving the first scheme of formulation, are common, such as reduction of aliphatic diazo-compounds and addition of Grignard reagents. Many reactions, such as the addition of unsaturated compounds, occur in conformity with the second scheme, and may be written :

$$R_2C:N:N + A=B \longrightarrow \begin{array}{c} R_2C \cdot N:N \\ A—B \end{array} \longrightarrow R_2C<\begin{array}{c} A \\ B \end{array}$$
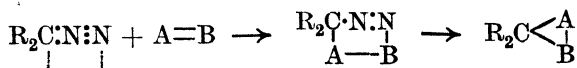
and the action of water, acids, alcohols, and amines proceeds in a similar manner. Comparison with the reactions of ketens enables a close analogy to be drawn.

The period covered by this division of the Report is from December 1921 to November 1922 inclusive, but the section on optical activity includes also the work of the previous year.

W. N. HAWORTH.

PART II.—HOMOCYCLIC DIVISION.

IN compiling this report the writer has endeavoured to adopt an impartial and unprejudiced point of view, but he is fully aware of the difficulties which may be encountered in such an attempt and, if there are occasionally signs of straying from the path, the only extenuating circumstance which can be urged in mitigation of the

[5] Langhans, *Z. ges. Schiess. u. Sprengstoffw.*, 1922, **17**, 9, 18, 26; *A.*, i, 328.
[6] *Helv. Chim. Acta*, 1922, **5**, 87; *A.*, i, 238.

offence is that in all probability an entirely neutral survey would also be lifeless and devoid of value. Both in volume and in sustained interest the work published during the year fully reaches the pre-war level and attention may be specially directed to the series of papers on tautomerism, ring-formation, and allied subjects which have been prosecuted in the laboratories at S. Kensington and recorded in papers which followed one another in quick succession with almost bewildering rapidity.

Constitution of Benzene.

The Dewar formula for benzene has been revived by C. K. Ingold,[1] who regards it as one of the phases in an equilibrated system of valency isomerides :

(I.)
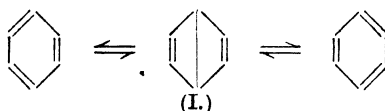
The argument is partly by analogy with the recently observed intra-annular tautomers (p. 113) and partly derived from a survey of the reactions of phenol and its derivatives.

This view would be contested by few if the para-linking were interpreted as amounting to a relatively weak partial valency only, but the suggestion is apparently advanced in a much more uncompromising form, to which there are obvious and serious objections. It is, for example, contrary to experience to assume that a substance of the formula I could be so stable to permanganate as are many derivatives of benzene. There is also the behaviour with ozone, the absence of dicyclic products of reduction processes, and, in general, the absence of any degradation product of benzene or its derivatives in which the carbon atoms in the para-position are found to be connected. It would be beside the mark to answer this criticism by assuming high reactivity of the para-bond, because in that case too high a standard of activity is set by the ethylene linkings. A conjugated system connecting two atoms is in many respects the equivalent of a direct bond and naturally, therefore, very many reactions can equally well be represented as due to the intervention of either. But the theory of reversible addition to conjugated systems involves the fewer inconsistencies and is a wider generalisation. Only one specific point can be touched upon and that concerns the relation of quinol to quinone. The scheme given is :
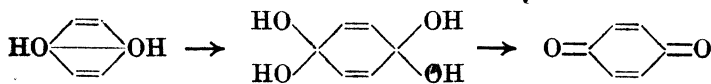
[1] *T.*, 1922, **121**, 1123.

This does not accommodate the fact that dihydric phenols may be oxidised to quinones by means of silver oxide or lead peroxide in dry ethereal or benzene solution,[2] and many other arguments could be quoted in support of the view that the relation between quinol and quinone is a directly reversible one involving the removal and addition of two hydrogen atoms. An extremely elegant synthesis of orcinol is described by Ingold in Part II of the series, the title of which is " Synthetic Formation of the Bridged Modification of the Nucleus." [3]

Ethyl β-methylmethanetriacetate (II) was converted by means of sodium or potassium in xylene solution into a mixture of substances from which it was possible to isolate ethyl 3-methyl*cyclo*butan-1-one-3-acetate (III). The question of the constitution of this substance is not discussed, and it must be assumed that there is some undisclosed reason why it cannot have the open-chain formula, $Me \cdot CO \cdot CH \colon CMe \cdot CH_2 \cdot CO_2Et$, apparently a possibility. The ester III was obtained in very small yield and was found to undergo transformation to orcinol (IV) under the influence of sodium in ether–benzene solution.

$$
\underset{(II.)}{
\begin{array}{c}
\text{CMe} \\
CH_2 \quad CH_2 \quad CH_2 \\
CO_2Et \quad CO_2Et \quad CO_2Et
\end{array}}
\qquad
\underset{(III.)}{
\begin{array}{c}
CH_2-CMe-CH_2 \\
CO-CH_2 \quad CO_2Et
\end{array}}
\qquad
\underset{(IV.)}{
\begin{array}{c}
\text{CMe} \\
CH_2 \quad CH_2 \\
CO \qquad CO \\
\text{CH}
\end{array}}
\qquad
\begin{array}{c}
\text{Me} \\
HO \quad OH
\end{array}
$$
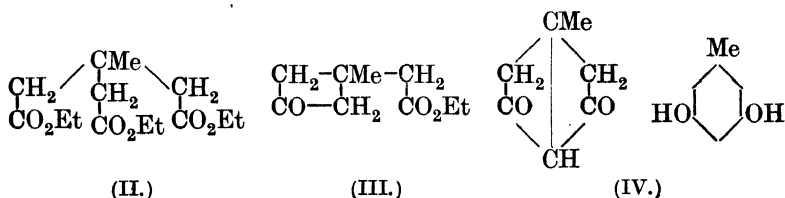
Synthetic evidence is, however, generally regarded as inadmissible in such cases, unless, indeed, two valency isomerides are sufficiently stable to exist independently as, for example, is the case with *cyclo*butene and butadiene. It should be stated that the above synthesis is not regarded by its originator as a complete proof of the occurrence of the bridged phase of the nucleus.

A new benzene model has been suggested by Fraser,[4] but it does not appear to satisfy the necessary structural conditions. Briefly, it is the most symmetrical possible arrangement of six tetrahedra which will fulfil the requirements of the facts of isomerism of substituted derivatives and also bring the groups in the ortho-position into closer space relationship than those in the meta- and para-positions. The solution of this problem in geometry leads to a " twisted " Ladenburg prism formula in which each carbon atom is attached to two others in the *m*-positions and to the carbon atom

[2] R. Willstätter and J. Parnas, *Ber.*, 1907, **40**, 1406; R. Willstätter and F. Müller, *ibid.*, 1908, **41**, 2580.

[3] C. K. Ingold, *T.*, 1922, **121**, 1143.

[4] R. Fraser, *ibid.*, 188.

in the p-position. It thus contains nine single bonds or, in the terminology of the octet theory, there are six octets connected by means of nine duplets. Adopting the hexagon convention in order to indicate the carbon atoms in o-, m-, and p-positions, the arrangement of valencies is as shown in the annexed figure, which closely resembles the stereographic projection of the model.

One of the chief of the many groups of facts which are at variance with this interpretation is concerned with the relations of aromatic and hydroaromatic compounds. Orientation in the benzene and *cyclo*hexane series is in many cases an independent process and the results are always in agreement with the supposition that no serious rearrangement in the mode of linking of the carbon atoms occurs when a benzene derivative is reduced. In Fraser's model the unbroken *cyclo*hexane rings are indicated by the figures 1, 2, 3, 4, 5, 6
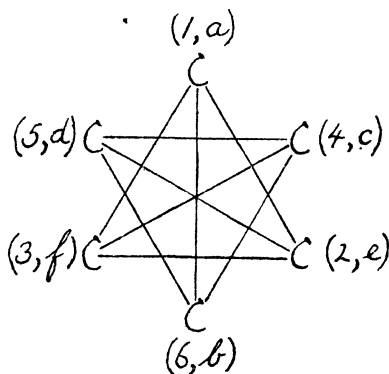
and letters a, b, c, d, e, f, and there may be other possibilities none of which represents the succession of atoms characteristic of the reduction products. Even in the formation of dihydro-derivatives it would be necessary to delete the nine bonds and replace them by entirely new ones and it is a severe strain on one's capacity for assimilation of new ideas. The tautomeric change of phloroglucinol into triketohexamethylene would similarly involve an alteration in position of each of the nine bonds. In terms of the prevailing version of the electronic theory of valency, the problem of the constitution of benzene becomes that of the disposition of eighteen electrons, twelve of which may be assumed to be involved in the formation of the ring. In regard to the remaining six, numerous suggestions have been made,[5] independently, but with points of

[5] H. Kauffmann, " Die Valenzlehre," p. 539; H. Stark, " Die Elektrizität in Chemischen Atom," p. 215; H. Pauly, *J. pr. Chem.*, 1918, [ii], **98**, 118; W. O. Kermack and R. Robinson, *T.*, 1922, **121**, 437; M. L. Huggins, *Science*, 1922, **55**, 679; *A.*, i, 997; *J. Amer. Chem. Soc.*, 1922, **44**, 1607; *A.*, i, 928; E. C. Crocker, *ibid.*, p. 1618; *A.*, i, 927.

contact especially in regard to the explanation of the laws of substitution. The further discussion of this highly speculative subject cannot be attempted here.

It will be recalled that, as the result of the X-ray analysis of crystals of naphthalene and other aromatic compounds, Sir William Bragg concluded that the characteristic hexagonal rings are puckered.[6] More recently, somewhat modified figures for the crystal molecules of benzene, naphthalene, and anthracene have been presented and are intended to show a solution which would be in agreement with the results so far obtained.[7] It is, at any rate, already clear that the carbon atoms in the individual crystal molecule do not lie in a plane. It is interesting to note that similar conclusions in regard to *cyclo*hexane rings have been reached as the result of a study of the influence of stereoisomeric *cyclo*hexane-diols on the conductivity of boric acid and of the behaviour of the glycols on condensation with acetone.[8] The chief obstacle to the acceptance of the view that this arrangement is a stable one, rather than a phase of an oscillation which may be suppressed in crystallisation or in the course of a reaction, lies in the fact that numerous cases of enantiomorphism should arise in substances hitherto regarded as composed of symmetrical molecules. Although its chief interest may possibly be in connexion with another matter, the opportunity may be taken to mention here the important achievement of the resolution of γ-6 : 6'-dinitrodiphenic acid (V) into optically active components.[9]

$$(\text{V.})\ ^{10} \qquad \underset{\text{CO}_2\text{H}}{\overset{\text{NO}_2}{\diagup}} \text{———} \underset{\text{NO}_2}{\overset{\text{CO}_2\text{H}}{\diagup}}$$
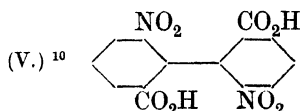
The resolution was carried out with the aid of brucine, and the acid from the less soluble salt had $[\alpha]_D = + 225°$ and exhibited a tendency to racemise. The significant feature which distinguishes this example of enantiomorphism from all others is, of course, that the cause of the asymmetry must be sought in some property of the nucleus. The authors point out that their results may be explained on the basis of alternative hypotheses, and the one which is apparently favoured is that the two nuclei are not coplanar. In other words, Kaufler's diphenyl configuration or some modification

[6] Presidential Address to the Physical Society, *Proc. Phys. Soc.*, 1921, **34**, 33.

[7] Sir William Bragg, *T.*, 1922, **121**, 2783.

[8] H. G. Derx, *Rec. trav. chim.*, 1922, **41**, 312; *A.*, i, 651.

[9] G. H. Christie and J. Kenner, *T.*, 1922, **121**, 614.

[10] Compare *Ann. Reports*, 1921, p. 88.

of this is indicated. Indeed the support which Cain's work in the diphenyl series lent to Kaufler's view led to the prediction now verified, that certain members of the group might be resolvable.[11] If this explanation is accepted, and it appears reasonable from every point of view, it follows that the bond connecting the two phenyl nuclei is not in the plane of either of the benzene rings [12] and this is most easily understood on the basis of the benzene configuration deduced by Bragg. But it may be pointed out that the juxta-position of two benzene rings in diphenyl and its derivatives is in some respects analogous to the packing of isolated molecules in the crystals and might conceivably have a similar effect in damping vibrations.

Orientation.

The fact that m-nitrotoluene gives as one product of nitration 2 : 3 : 6-trinitrotoluene is of interest since, in this case, the nitroxyl enters every possible position o- and p- to the methyl group but apparently not at all m- to the nitro-group.[13] It is remarkable that o-methoxybenzoic acid should yield, on nitration, along with the normal products, no less than 27 per cent. of 4-nitro-2-methoxy-benzoic acid (I),[14] because whilst m-directive groups are almost always also o-directive, it is very rarely that substitution in the m-position occurs with respect to a pronouncedly o-p-directive group. One of the very few instances on record may now be deleted from the literature, since it has been found that the acid obtained by Griess by the nitration of m-hydroxybenzoic acid and regarded by him as the 5-nitro-acid (II) is in reality 6-nitro-m-hydroxybenzoic acid and substitution occurs exclusively in the o- and p-positions with respect to hydroxyl. It is interesting that chlorination occurs in positions 2 and 6 but bromination leads only to the formation of 4-bromo-m-hydroxybenzoic acid.[15] In the nitration of nitroacetotoluidides, two instances have been recorded in which the presence or absence of sulphuric acid very greatly influences the position taken up by the entering substituent.

(I.)   (II.)
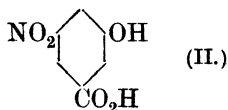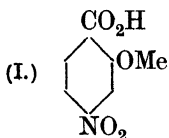
[11] H. King, P., 1914, **30**, 250; J. F. Thorpe, T., 1921, **119**, 535.

[12] J. Kenner, Nature, 1922, **109**, 581; A., i, 533.

[13] O. L. Brady, T., 1922, **121**, 328.

[14] V. Froelicher and J. B. Cohen, ibid., 1652.

[15] P. H. Beyer, Rec. trav. chim., 1921, **40**, 621; A., i, 37.

In the following scheme, the main products are indicated.

Me   Me   Me

NO_2⟨ ⟩NHAc $\xleftarrow{HNO_3}$ NO_2⟨ ⟩NHAc $\xrightarrow[HNO_3]{H_2SO_4}$ NO_2 / NO_2⟨ ⟩NHAc   (16)
NO_2

Me   Me   Me

⟨ ⟩NO_2 NO_2 $\xleftarrow{HNO_3}$ ⟨ ⟩NO_2 $\xrightarrow[HNO_3]{H_2SO_4}$ NO_2⟨ ⟩NO_2 (17)
NHAc   NHAc   NHAc
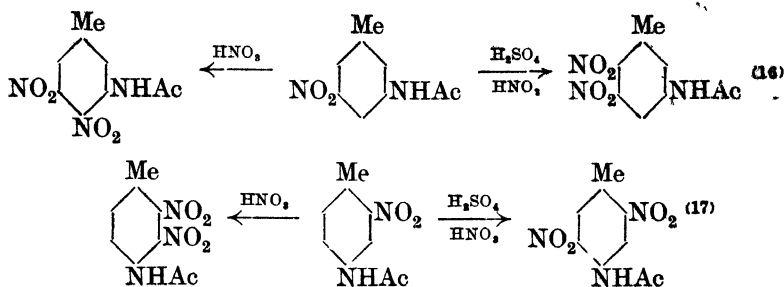
In sulphonation of naphthols and naphthylamines the apparently perplexing results can readily be collated with the orientation rules developed in the benzene series if certain of the peculiarities of naphthalene, such as the reactivity of hydrogen atoms in the α-positions, are taken into account. Thus, by analogy with phenol, the points of attack in β-naphthol should be positions 1, 3, 6, and 8, and these are the positions occupied by sulphonic radicles in the well-known, technically useful acids prepared by direct sulphonation. It is now shown that bromination of β-naphthol leads to the 1-, 1 : 6-, 1 : 3 : 6-, and 1 : 3 : 4 : 6-bromo-derivatives.[18] The formation of the last substance involves attack of position 4, which is m- to hydroxyl, but it is also o-p- to bromine, so that the result is not surprising.

Reactions and Preparative Methods.

Reduction.—Stereoisomeric *cyclo*hexanetriols are obtained from each of the three trihydroxybenzenes by catalytic reduction in aqueous or alcoholic solution at 140° under pressure. The catalyst used is nickel.[19] The usefulness of Rosenmund's process for the preparation of aldehydes by catalytic reduction of acid chlorides is well illustrated by the preparation of gallaldehyde in quantity by way of its triacetate,[20] and the method has also been successfully applied to a number of chlorides of dibasic acids, for example, *iso*phthalyl and terephthalyl chlorides.[21] The reduction of nitrobenzene in neutral media by means of hydrogen in presence of

[16] O. L. Brady, J. N. E. Day, and W. J. W. Rolt, *T.*, 1922, **121**, 526.

[17] J. Scott and R. Robinson, *ibid*, 844.

[18] H. Franzen and G. Stäuble, *J. pr. Chem.*, 1921, [ii], **103**, 352; *A.*, i, 450.

[19] J. B. Senderens and J. Aboulenc, *Compt. rend.*, 1922, **174**, 616; *A.*, i, 337.

[20] K. W. Rosenmund and E. Pfannkuch, *Ber.*, 1922, **55**, [B], 2357; *A.*, i, 1030.

[21] K. W. Rosenmund, F. Zetzsche, and C. Flütsch, *ibid.*, 1921, **54**, [B], 2888; *A.*, i, 39.

palladised animal charcoal at the ordinary temperature leads to the production of β-phenylhydroxylamine in a yield of 80 per cent.[22]

Ammonium sulphite has been recommended as a reducing agent applicable to the preparation of arylhydrazines, particularly those containing nitro-groups, from related diazonium salts.[23]

Nitration.—Quite a novel nitrating agent has been found in anhydrous pyridinium nitrate, applied in presence of excess of pyridine. Naphthalene yields α-nitronaphthalene (40 per cent.), and anthracene yields 9-nitroanthracene (70 per cent.), when treated in this manner.[24] The nitration of quinol dibenzoate never yields a mononitro-derivative but instead 2 : 6-dinitroquinol dinitrobenzoate. When, however, 2-nitroquinol dibenzoate was obtained by another process, it was found to be impossible to introduce a second nitroxyl into the quinol nucleus. This interesting observation can only be explained by the abnormal reactivity of a molecule at the moment of its formation.[25]

Halogenation.—A very powerful chlorinating agent is produced in a mixture of sulphur monochloride and sulphuryl chloride by the addition of anhydrous aluminium chloride and appears to be an aluminium sulphur chloride of the composition, $Al_2S_2Cl_8$. In conjunction with sulphuryl chloride, this substance readily changes chlorobenzene into dichlorobenzenes, tetrachlorobenzene, and hexachlorobenzene in successive stages.[26] An investigation of the products formed by the chlorination of benzoyl chloride in presence of anhydrous ferric chloride has shown that the percentages of the isomerides obtained are *o*- 14·5, *m*- 83·5, *p*- 2·0, and details are given of the preparation of pure *m*-chlorobenzoic acid by this method.[27] Important advances from the preparative point of view have also resulted from a research on the chlorination of the three toluoyl chlorides at temperatures varying from 160—240°.[23] In this case, substitution naturally occurs in the methyl group and substances of the types

$$C_6H_4{<}^{CH_2Cl}_{COCl}, \quad C_6H_4{<}^{CHCl_2}_{COCl}, \quad \text{and} \quad C_6H_4{<}^{CCl_3}_{COCl}$$

are obtained in good yield. The *o*-, *m*-, and *p*-ω-dichlorotoluoyl

[22] K. Brand and J. Steiner, *Ber.*, 1922, **55**, [*B*], 875; *A.*, i, 536.

[23] W. Davies, *T.*, 1922, **121**, 715.

[24] M. Battegay and Ph. Brandt, *Bull. Soc. chim.*, 1922, [iv], **31**, 910; *A.*, i, 1001.

[25] F. Kehrmann, M. Sandoz, and R. Monnier, *Helv. Chim. Acta*, 1921, **4**, 941; *A.*, i, 33.

[26] O. Silberrad, *T.*, 1922, **121**, 1015.

[27] E. Hope and G. C. Riley, *ibid.*, 2510.

[28] W. Davies and W. H. Perkin, *ibid.*, 2202.

chlorides on digestion with milk of lime or chalk in an inert atmosphere yield the three phthalaldehydic acids in a pure condition, and this is the simplest method of preparation of these valuable substances. Somewhat unexpectedly it was found possible to hydrolyse the three ω-trichlorotoluoyl chlorides by careful treatment with formic acid and so to obtain the *o*-, *m*-, and *p*-ω-trichlorotoluic acids, $CCl_3 \cdot C_6H_4 \cdot CO_2H$, which are relatively stable, crystalline substances.

Alkylation.—*cyclo*Hexanol may be converted into a stereoisomeride of the known 2-methyl*cyclo*hexanol (obtained by catalytic reduction of *o*-cresol) by conversion into *cyclo*hexene, oxidation of the latter by means of perbenzoic acid in chloroform solution with production of the *oxide*, and finally by the action of magnesium methyl iodide on this substance.[29]
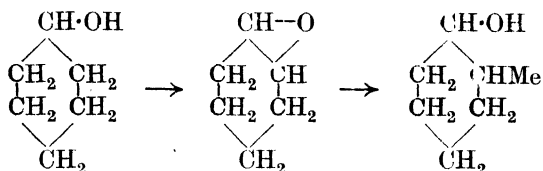
Another ingenious alkylation process is illustrated by the preparation of β-phenyl-αα-dimethylpropionic acid from β-phenylpropionic acid. This substance is first converted into α-hydrindone by Kipping's method, and the ketone alkylated by means of sodamide and methyl iodide. The product is 2 : 2-dimethylindan-1-one (I) and this may be decomposed by sodamide with formation of the amide of the desired acid (II).
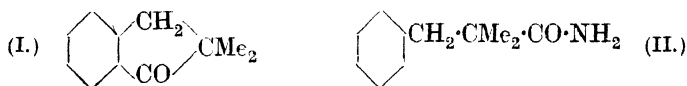
The process is rendered more generally applicable to an acid $R' \cdot CH_2 \cdot CO_2H$ by the stages $R' \cdot CH_2 \cdot COCl$, $R' \cdot CH_2 \cdot COPh$, $R' \cdot CR_2 \cdot COPh$, $R' \cdot CR_2 \cdot CO \cdot NH_2$.[30] On heating ethylene chlorohydrin with toluene-*p*-sulphonyl chloride, β-chloroethyl toluene-*p*-sulphonate, $C_6H_4Me \cdot SO_2 \cdot O \cdot CH_2 \cdot CH_2Cl$, is obtained in a yield of more than 90 per cent. This ester is a valuable agent for the introduction of the chloroethyl group into phenols and amines. The method is far more convenient and gives much better yields than those depending on the use of ethylene halides.[31]

Condensations.—The use of sulphoacetic acid, prepared by

[29] M. Godchot and P. Bédos, *Compt. rend.*, 1922, **174**, 461; *A.*, i, 334.

[30] A. Haller and E. Bauer, *Ann. Chim.*, 1921, [ix], **16**, 340; *A.*, i, 258.

[31] G. R. Clemo and W. H. Perkin, *T.*, 1922, **121**, 642.

mixing acetic anhydride and sulphuric acid, as a synthetical agent continues to give results of interest. Under specified conditions, guaiacol may be converted by this reagent into acetylisoaceto-vanillone (III),[32] whilst pyrogallol 1 : 3-dimethyl ether is acetylated in the nucleus even when it is heated with acetic anhydride and a few drops of sulphuric acid. In this case, the product is 3-acetoxy-2 : 4-dimethoxyacetophenone (IV).[33]

 (III.)   (IV.)

It is generally believed that the mechanism of substitution in the aromatic series comprises two main stages; an addition and then a fission of the additive product. The second reaction is, however, usually so rapid that the initial phases of the process are difficult to recognise, although this is not invariably the case. In the olefine series, the addition is more facile and the fission more difficult than in the aromatic series. Advantage has been taken of this circumstance in connexion with some experiments on the mechanism of the Friedel-Crafts' reaction. It has been shown that, under the influence of aluminium chloride, acetyl chloride unites with cyclohexene with the production of 2-chlorocyclohexyl methyl ketone (V), which is isolable and convertible by the further action of aluminium chloride in carbon disulphide solution into tetrahydroacetophenone (VI).[34]

 (V.)   (VI.)
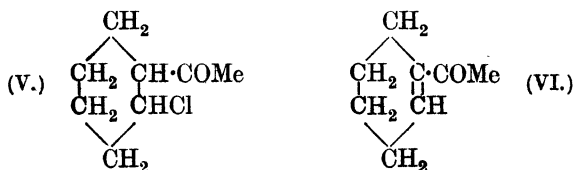
The function of the aluminium chloride is identical in both stages and is considered to be concerned with the weakening of the link between carbon and chlorine. A peculiar application of the catalytic activity of aluminium chloride is the elimination of hydrogen from aromatic nuclei. This is always effected in presence of nitrobenzene, which exercises a specific influence. The best known examples are the syntheses of complex polynuclear compounds due to Scholl and his collaborators, for example, that of pyranthrone

[32] W. Schneider and E. Kraft, *Ber.*, 1922, **55**, [*B*], 1892; *A.*, i, 750.

[33] K. Brand and H. Collischon, *J. pr. Chem.*, 1921, [ii], **103**, 329; *A.*, i, 452.

[34] H. Wieland and L. Bettag, *Ber.*, 1922, **55**, [*B*], 2246; *A.*, i, 1033.

from dibenzoylpyrene by intramolecular condensation. The reaction is capricious in its vagaries, but has now been applied to certain simple compounds. Thus benzil yields phenanthraquinone (25 per cent.) and α-naphthyl ethyl ether yields 4 : 4′-diethoxy-1 : 1′-dinaphthyl (70 per cent.).[35] Attempts have been made to replace the nitrobenzene by azobenzene, but this is not possible in most cases. Aminodiphenyl is obtained, however, in a yield of 70—80 per cent. by the regulated action of aluminium chloride at 60° on a mixture of benzene and azobenzene.[36] The explanation advanced includes four stages, which are summed up in the equation

$$\text{PhN:NPh} + 2C_6H_6 = 2C_6H_4Ph \cdot NH_2.$$

On account of the excellent yields and the relation of the products to naturally occurring compounds the synthesis of β-keto-bases from ketones, formaldehyde, and amine salts is noteworthy. A typical instance is afforded by the preparation of ω-dimethyl-aminopropiophenone, obtained as its hydrochloride by heating together equivalent quantities of acetophenone, paraformaldehyde, and dimethylamine hydrochloride in concentrated alcoholic solution :

$$\text{COPhMe} + CH_2O + NHMe_2 \longrightarrow COPh \cdot CH_2 \cdot CH_2 \cdot NMe_2.^{37}$$

Molecular Rearrangements.

Admittedly the allocation of specific configurations to stereo-isomeric oximes rests on a slender foundation, and one of the sign-posts has, it now appears, been turned in the wrong direction. The unwarranted assumption that in the Beckmann change groups in a cis-position are transposed has been proved to be erroneous by J. Meisenheimer.[38] 3 : 4 : 5-Triphenylisooxazole (I) is oxidised by chromic acid, or by ozone, with formation of benzoyl-β-benzil-monoxime (II).

(I.) PhC——CPh   PhC·COPh   (II.)
        ‖   ‖   ‖
        N·O·CPh   N·OBz

This independent and probably trustworthy determination of configuration involves the alteration of the formulæ, at present accepted, of the dioximes of benzil; the α-dioxime is III and the β-modification is IV, no change being required in regard to the γ-variety.

(III.) PhC·CPh   PhC————CPh (IV.)
          ‖ ‖   ‖   ‖
        HO·N N·OH   N·OH HO·N
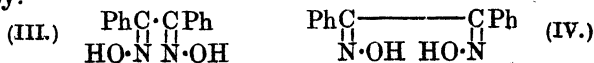
[35] R. Scholl and G. Schwarzer, Ber., 1222, 55, [B], 324; A., i, 331; R. Scholl and C. Seer, ibid., 630; A., i, 336.
[36] R. Pummerer and J. Binapfl, ibid., 1921, 54, [B], 2768; A., i, 24.
[37] C. Mannich and G. Heilner, ibid., 1922, 55, [B], 356; A., i, 351; C. Mannich and D. Lammering, ibid., 3510.
[38] Ibid., 1921, 54, B], 3206; A., i, 152.

These corrections should be noted by writers of text-books and constitute an excellent example of the prudence of employing non-committal prefixes to distinguish stereoisomerides. The Beckmann transformation must now be represented as occurring in accordance with the scheme :

$$\text{R—C—R}' \quad \rightarrow \quad \underset{\text{N—R}'}{\text{HO—C—R}} = \text{R·CO·NHR}'.$$
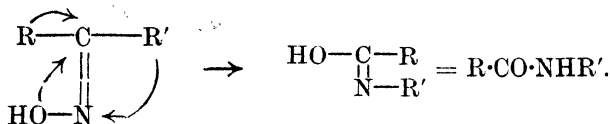
In continuance of earlier work, a comparative study has been made of the "semibenzene" hydrocarbons and their aromatic isomerides.[39] The semibenzenes have the lower densities and the higher molecular refractions and dispersions. The simplest member of the series is 1 : 1-dimethyl-4-methylene-$\Delta^{2:5}$-*cyclo*hexadiene (V), which passes very readily into ψ-cumene (VI), with development of heat, when a drop of hydrochloric acid is added to its solution in acetic acid.

(V.) Me_2⟨=⟩=CH$_2$ Me⟨Me⟩Me (VI.)
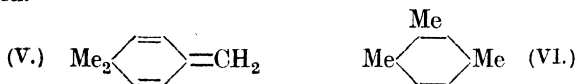
This transfer of the alkyl group to the adjacent carbon atom represents the normal occurrence, but instances of migration to the meta-position are not lacking. Thus the semibenzene VII is changed by warming with a mixture of acetic and sulphuric acids into pentamethylbenzene (IX). The possibility might be queried that this is a double migration through the intermediate stage VIII or a related hydrated compound.

Me₂⟨=⟩=CH₂   CH₂=⟨Me₂⟩Me   Me⟨Me Me⟩Me
Me   Me   Me
(VII.)   (VIII.)   (IX.)
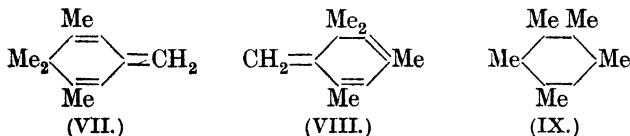
In the transformation of methylaniline hydrochloride into *p*-toluidine hydrochloride the main factor is found to be the temperature employed, and the course of the change is but little affected by the addition of salts such as zinc chloride or aluminium chloride. At 310°, there is notable production of dimethylaniline, and this tends to confirm the view that the migration is due to successive reactions, the methylaniline hydrochloride decomposing into aniline and methyl chloride, which react with formation of the original substances (reversible), of dimethylaniline (reversible), and of

[39] K. von Auwers and K. Ziegler, *Annalen*, 1921, **425**, 217; *A.*, i, 119.

p-toluidine (irreversible).[40]   A long paper [41] has been published by P. Jacobsen describing further developments of his exhaustive investigations of the isomeric changes of hydrazo-compounds.   On the whole, the results resemble those with which we are already familiar, but the following points may be mentioned.   If an ortho-position is free, di-*p*-substituted hydrazobenzenes yield *o*-semidines which, in case the substituents are different, have one of two formulæ as indicated below :
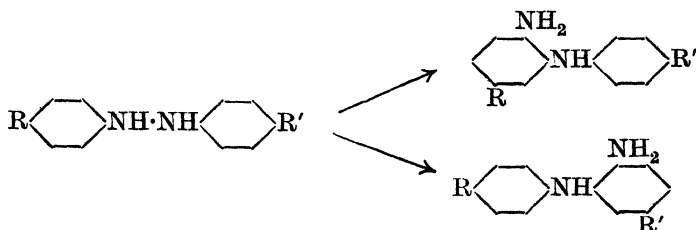
In no instance were both possible *o*-semidines isolated.   If the convention is adopted that the amino-group of the semidine occurs in the *p*-position to that one of the two *p*-substituents in the hydrazo-compound which has the greater " directing power " in the transformation, then, of all the groups examined, ethoxyl is the most powerful and methyl comes next in order.   When R is acetoxyl, a *p*-semidine is formed by displacement of the group; thus 4'-acetoxy-4-methylhydrazobenzene (X) yields the *o*-semidine (XI) and the *p*-semidine (XII).|
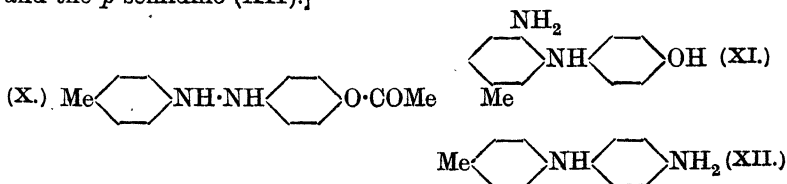
This extrusion of oxygen, directly united to the aromatic nucleus, is a very rare phenomenon.   No example of the *o*-benzidine change was encountered in the benzene series, but its occurrence in the naphthalene group was confirmed.   The following comparison is interesting :
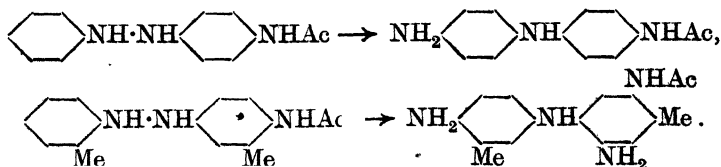
[40] E. Beckmann and E. Correns, *Ber.*, 1922, **55**, [*B*], 852; *A.*, i, 535.
[41] *Annalen*, 1922, **427**, 142; *A.*, i, 589.

In the second case figured, the p-semidine is also formed but in very small relative amount. Migration of a benzoyl group is proved to occur in the course of the synthesis of benzoylmethylenedioxy-benzoin by the action of an alcoholic solution of sodium ethoxide on a mixture of benzoylmandelonitrile and piperonal : [42]

$$CHPh(OBz)\cdot CN + CHO\cdot C_6H_3\vdots O_2CH_2 \rightarrow COPh\cdot CH(OBz)\cdot C_6H_3\vdots O_2CH_2.$$

This confirms Lapworth's theory that the production of benzoin in the usual manner depends fundamentally on the aldol-like condensation of benzaldehyde and mandelonitrile.

Reactivity of Halogen Atoms in Carbon Compounds.

The reactivity of halogen is of two main types which may coexist but are exhibited to an unequal degree in any one compound. The atom is in some cases readily replaced by such groups as —OH, NH_2, and in other instances it is essentially reducible and oxidising. The extreme hydrolysable type is represented by chlorine in the acid chlorides. This, it should be noted, is also reducible under the correct conditions, but the reaction is far from being as characteristic as that of replacement by hydroxyl. The reducible type is found in the hypochlorites, in substances containing the group —NCl— such as the N-chlorosulphonamides, and in $\alpha\alpha$-dihalogenated β-di-ketones. In these cases replacement of the halogen by hydroxyl is still possible, but is often a very difficult operation. Adherents of the various brands of polarity theories speak of the halogen as negative or positive and this is at least a useful classification of a wide range of phenomena. It is perhaps a little more accurate and certainly more non-committal to regard the atom to which the halogen is attached as positive and negative respectively. A very interesting series of observations has been made on the in-fluence of substituents in the benzene ring on the mobility of chlorine in the shortest side chain.[43] The reaction measured was the hydrolysis of the various benzyl chlorides and the influence of the groups was found to be in the order : p-Me$>o$-Me$>m$-Me$>$H$>$$p$-Cl$>o$-Cl$>m$-Cl$>m$-NO$_2>o$-NO$_2>p$-NO$_2$.

Now the groups Me, H, Cl, NO_2 represent a descending series in regard to the electropositive character of the constituent atoms and the results show that, independent of the position of the substituent, the more electropositive is the molecule the quicker is the hydrolysis. This is an example of the *general polar* effect, the direction of which is explained by the consideration that the reaction is fundamentally, under the conditions employed, an attack on the molecule by

[42] H. Greene and R. Robinson, *T.*, 1922, **121**, 2182.
[43] S. C. J. Olivier, *Rec. trav. chim.*, 1922, **41**, 301; *A.*, i, 646.

negative hydroxyl ions. In a similar investigation of the speed of synthesis of sulphones by the condensation of benzene with substituted benzenesulphonyl chlorides, the series was expanded to : $Me > H > I > Br > Cl > NO_2$. But on comparing the effect of position of the substituent on the reactivity, it will be seen that $—CH_3$ and Cl— exercise their greatest influence from the p- and o-positions, whilst m-NO_2-benzyl chloride is more reactive than its isomerides. This reversal in passing from groups which are negative on the basis of the theory of *alternating* polarity, to a group which, on the same grounds, must be considered positive is in agreement with the work of Lapworth and Shoesmith (see below) and the whole research throws some light on the relative importance to be attached to the general and alternate polar effects. If the methoxy-compounds had been included in the series, there is little doubt that o- and especially p-methoxybenzyl chloride would have proved the most reactive of the substances investigated. This is to be expected because there is strong evidence that methoxyl is conjugated with the nucleus, a circumstance which allows the alternate effect to overpower the general effect and throws such groups as methoxyl and amino out of their natural order. If the correlation of the two types of reactivity of halogen with polarity effects is well founded, then it must follow that positional influences which facilitate hydrolysis of alkyl or aryl halides will render reduction more difficult and vice versa. Again, the general effect must be eliminated by comparing isomerides only. Such a comparison has been made of the three methoxybenzyl bromides and the results are in excellent agreement with the theory.[44] The effect of the negative methoxyl group on the bromine atom is illustrated in the following expressions, in which the signs have a purely relative significance :

It will be seen that in the o- and p-compounds the result is to enhance the natural polarity of the bromine, whereas the reverse is the case in m-methoxybenzyl bromide. Therefore o- and p-methoxybenzyl bromides should be more readily hydrolysed than the m-isomeride, and this was found to be the case to a very striking extent. Numerous examples of the high reactivity of bromine in a side chain p- to methoxyl were, however, already known and the second part of the prediction, that the m-methoxybenzyl bromide

[44] A. Lapworth and J. B. Shoesmith, *T.*, 1922, **121**, 1391.

should be found to contain the more reducible halogen, is therefore all the more valuable as a test of the hypothesis because it could not have been made by analogy with known reactions and without considerations based on induced polarities. Experiments on the reduction of the methoxybenzyl bromides with hydrogen iodide showed that actually the *m*-derivative was the most readily attacked. This double verification of anticipated effects is not to be neglected in assessing the value of the theory in connexion with the problems of reactivity and mechanism of reactions. Halogen atoms in the *o*- or *p*-positions with respect to a strongly negative atom or group in the aromatic nucleus should evince positive polar character and this has already been shown by numerous investigators to be the case so far as reducibility is concerned. Additional evidence is supplied by the behaviour of certain iodinated benzene derivatives.[45] 3-Iodo-*p*-toluidine, *p*-iodoaniline, and 3-iodo-*p*-hydroxybenzoic acid are decomposed by boiling with 10 per cent. hydrochloric acid in such a way that the iodine is partly replaced by hydrogen and in compensation there is production of di- and tri-iodo-derivatives. Aceto-3-bromo-*p*-toluidide behaves in a similar manner. This substituting action in presence of acids is typical of the behaviour of positive halogen and is presumably due to elimination in the form $\overset{+}{\text{hal}}(\overset{-}{\text{OH}})$, as the result of the union of the negative carbon atom, or other atom to which the halogen is attached, with a hydrogen ion. Some significant examples have been previously recorded and perhaps the most interesting in the aromatic series is the formation of 3-bromo-2-aminoanthraquinone either by heating 1-bromo-2-amino-anthraquinone alone or a mixture of 2-aminoanthraquinone with 1 : 3-dibromo-2-aminoanthraquinone. The former reaction is the migration of bromine to a more stable position in the molecule and may be compared with the well-known change of ethyl α-bromo-acetoacetate into ethyl γ-bromoacetoacetate which occurs in presence of traces of hydrobromic acid.[46] The simplest explanation[47] takes cognisance of the highly positive character of the bromine atom in the α-position, where it is under the influence of both the carbonyl and carbethoxyl groups, and involves the stages :

$$CH_3 \cdot CO \cdot CHBr \cdot CO_2Et + HBr \rightleftharpoons CH_3 \cdot CO \cdot CH_2 \cdot CO_2Et + Br_2 \rightarrow$$
$$CH_2Br \cdot CO \cdot CH_2 \cdot CO_2Et + HBr.$$

An alternative mechanism which has been suggested[48] is the following :

[45] B. H. Nicolet, *J. Amer. Chem. Soc.*, 1921, **43**, 2081; *A.*, i, 121.

[46] A. Hantzsch, *Ber.*, 1894, **27**, 356, 3168; M. Conrad, *ibid.*, 1896, **29**, 1042.

[47] A. Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 8.

[48] G. T. Morgan and H. D. K. Drew, *T.*, 1922, **121**, 928.

$$O{:}C{<}^{CH_3}_{CHBr}{/}^{CO_2Et} \rightarrow O{:}C{<}^{CH_2\text{---}}_{CHBr}{>}C{<}^{OEt}_{OH} \rightarrow$$

$$O{:}C{<}^{CH_2}_{CH_2Br}{\diagdown}CO_2Et$$

This is untenable because in the similar rearrangement of ethyl α-bromomethylacetoacetate, $CH_3{\cdot}CO{\cdot}CMeBr{\cdot}CO_2Et \longrightarrow CH_2Br{\cdot}CO{\cdot}CHMe{\cdot}CO_2Et$, the scheme involves transference of methyl as well as of bromine and the product should then have the constitution $CHBrMe{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, which does not appear to be the case.[49] There is no very cogent reason for supposing that substitutions by positive halogen must always depend on successive reactions and on the intervention of acids. Thus Woul has shown that acetobromoamide is a useful brominating agent and he regards the reaction as occurring directly between the molecules concerned and involving the interchange of hydrogen and bromine.[50] On the other hand, an ingenious process of regulated chlorination by means of N-chloroacetanilide and hydrochloric acid in small but definite concentration is based on a directly contrary assumption.[51] The two views are not irreconcilable nor in any way contradictory and both are entertained by Orton in connexion with different migration phenomena. Thus the direct substitution is analogous to the transformation of phenylnitroamine into o-nitroaniline and the indirect to the conversion of the N-chloroacetanilides into the nuclear-substituted isomerides. In order to avoid the formation of hydrobromic acid in the course of bromination, it is now proposed [52] to employ dibromodimethyldihydroresorcinol as a brominating agent. This substance is reduced with uncommon ease and even by the action of dilute aqueous sodium hydroxide. It reacts quantitatively with dimethylaniline in the following sense :

$$\underset{}{\overset{NMe_2}{\bigcirc}} + Br_2C{<}^{CO{\cdot}CH_2}_{CO{\cdot}CH_2}{>}CMe_2 = \underset{Br}{\overset{NMe_2}{\bigcirc}} + BrC{<}^{OH\diagdown C\text{---}CH_2}_{CO{\cdot}CH_2}{>}CMe_2$$

As the enolic monobromo-derivative can be recovered and used again, the method may have practical value. Gupta and Thorpe do not adopt the view that the reactivity of the bromine exhibited in this reaction is due to its positive polar character, but prefer the hypothesis that the bromine is mobile because it inhibits a tautomeric process involving the keto-groups. There is a tendency to acquire

[49] M. Conrad and A. Kreichgauer, *Ber.*, 1896, **29**, 1042.
[50] *Ibid.*, 1919, **52**, [*B*], 51.
[51] K. J. P. Orton and H. King, *T.*, 1911, **99**, 1185.
[52] B. M. Gupta and J. F. Thorpe, *ibid.*, 1922, **121**, 1896.

a hydrogen atom necessary for tautomerism, and earlier examples of the application of this theory will be recalled. In the Reporter's opinion, both views are correct and are reconciled by the consideration that the system acquires its hydrogen atom by union of the latter with oxygen so that an enol is the first product. Thus the fundamental factor is the affinity of oxygen for hydrogen and few chemists will find it difficult to equate this with the negative electrochemical character of oxygen and the positive character of hydrogen. The hydrogen is probably acquired as a proton which attaches itself to the free electrons of the oxygen octets; the molecule thus becomes positively charged and recovers neutrality by reversing the process, acquiring an electron (potassiobenzophenone ?) or as an important alternative by ejecting some other atom in a positively charged condition. In keto-enol tautomerism catalysed by hydrogen ions, we have the stages :

$$\text{(II)}\quad O{=}C{-}\overset{|}{C}{-}H \underset{}{\overset{}{\rightleftarrows}} \text{(II)}{\cdots}O{=}\overset{|}{C}{=}C{\cdots}H{\cdots} \underset{}{\overset{}{\rightleftarrows}} H{-}O{-}\overset{|}{C}{=}\overset{|}{C}\quad\text{(II)}$$

This may be compared with the following scheme in which the atom liberated is Br +, that is to say, bromine in a form which could combine with a hydroxyl ion to form hypobromous acid :

$$\text{(II)}\quad O{=}C{-}\overset{|}{C}{-}Br \rightarrow \text{(II)}{\cdots}\overset{-}{O}{=}\overset{+}{C}{=}\overset{+}{\overset{|}{C}}{\cdots}\overset{+}{Br}{\cdots} \rightarrow H{-}O{-}\overset{|}{C}{=}\overset{|}{C}\quad\overset{+}{Br}$$

The tendency towards a more even distribution of valency is the driving force in the reaction and this is carried into effect by a process of conjugation, using that term in its wider meaning of re-distribution of affinity through a chain of atoms. On this interpretation it is seen that " the tendency to acquire a hydrogen atom necessary for tautomerism " is a phrase which accurately represents the phenomenon and is not at all inconsistent with the view that the bromine exhibits positive polarity. In any particular case of double decomposition, the actual charges mentioned above need not be acquired, because the interchange of hydrogen and bromine will be synchronous. Probably too, both oxygen atoms in the diketone attract the hydrogen and this can easily be represented with the aid of partial valencies. It should be emphasised that the alternate labelling of atoms in a chain with + and − signs is never intended to indicate the mechanism of the effect, which, as in the example under discussion, is often the result of conjugation. Further interesting substitution reactions due to positive halogen have been encountered in a study of the action of nitrogen trichloride on aromatic hydrocarbons.[53] Toluene is

[53] G. H. Coleman and W. A. Noyes, J. Amer. Chem. Soc., 1921, **43**, 2211; A., i, 133.

converted into benzyl chloride, monochlorotoluenes, and more highly chlorinated compounds. At the same time, some N-chloro-aminotoluene derivatives are formed. Bromotrinitromethane contains a highly positive bromine atom and in aqueous hydrobromic acid solution is able to change phenol into its tribromo-derivative.[54] Reduction by titanous salts and oxidation of hydrazine with formation of nitrogen have been applied as tests for positive halogen, and an extensive comparative study of the effect of constitution on the property has been made.[55] The results are in very good agreement with the theory of induced alternate polarities of atoms in a chain, although some few details connected with degree of reactivity are not yet satisfactorily explained. This is not surprising, and it should be stated that, on account of the complexity of the factors which control the speed of reactions, the polarity theory cannot be successfully used to interpret relative reaction velocities except in carefully chosen cases. The chief necessary precautions are the avoidance of cases where the general polar effect and steric considerations are likely to be of importance and it is also desirable that the mechanism of the reaction should be known to a first approximation. One of the anomalous observations noted above is that dichloroacetylacetone, $COMe \cdot CCl_2 \cdot COMe$, does not oxidise hydrazine under the specified conditions, whereas ethyl dichloro-malonate, $CCl_2(CO_2Et)_2$, readily does so. The explanation given is based on the larger number of key oxygen atoms in the latter substance; but this leads to inconsistencies, as pointed but by Gupta and Thorpe (*loc. cit.*), and indeed carbonyl is universally regarded as a more activating group than carbethoxyl.

Triphenylmethyl and Related Subjects.

The electrical conductivity of solutions of triarylmethyl bromides in sulphur dioxide or hydrocyanic acid is comparable with that of aqueous solutions of potassium hydroxide and shows little variation among individuals. The molecular conductivities of the chlorides, however, are not so high and diphenyl-α-naphthylmethyl chloride is a better conductor than diphenyl-β-naphthylmethyl chloride and this again than triphenylmethyl chloride. The order is that of the ease of dissociation of the corresponding hexa-arylethanes into the free radicles and also of the conductivity of the free radicles themselves. Diphenyl-β-naphthylmethyl is obtained in the usual manner and the hexa-arylmethane, a pale yellow, crystalline powder,

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[54] T. Henderson and A. K. Macbeth, *T.*, 1922, **121**, 892.

[55] Henderson and Macbeth, *loc. cit.*; E. L. Hirst and A. K. Macbeth, *T.*, 1922, **121**, 904, 2169; H. Graham and A. K. Macbeth, *ibid.*, 1109; A. K. Macbeth, *ibid.*, 1116.

m. p. 135—140°, is found by the cryoscopic method to be dissociated from 15 to 50 per cent. in eight solvents ranging in freezing point from −22° to + 80°. The changes in colour of solutions of this substance due to alterations in concentration and temperature are by no means parallel to the changes in extent of dissociation. This shows that the equilibrium system is more complex than has often been assumed. It is suggested that in addition to dissociation there is also tautomerisation of the benzenoid radicle into a quinonoid modification.[56] It is perhaps well to note at this point that although to crystalline substances are now often given the names of the radicles produced in solution, the relation between the two states remains highly problematical. An interesting contribution to the subject is concerned with the preparation of pentaphenylethyl.[57] Sodium triphenylmethyl in ethereal solution is treated with benzophenone chloride, the containing vessel being filled with nitrogen. The products are pentaphenylethyl and triphenylmethyl and on concentration of the filtered liquid the former separates in coarse crystals and can be largely mechanically separated from the hexaphenylethane by swirling and decantation and completely by washing with ether.

$$2Ph_3CNa + CPh_2Cl_2 = Ph_3C \cdot CPh_2 + Ph_3C + 2NaCl.$$

Pentaphenylethyl forms golden-yellow crystals with a metallic glance and is almost entirely unimolecular in solution. Triphenyl-biphenylene-ethyl, $Ph_3C \cdot C \cdot C_6H_4 \cdot C_6H_4$, is similarly prepared from sodium triphenylmethyl and fluorenone chloride. It occurs in large, violet prisms and is wholly unimolecular in solution. The course of the decomposition of phenylazotriphenylmethane and of substituted derivatives has been examined with the object of determining whether free radicles are formed in the process or not.[58] Thus the production of tetraphenylmethane (Gomberg) might proceed according to the alternative schemes :

(A) $Ph \cdot N = N \cdot CPh_3 \longrightarrow Ph \cdot + N_2 + \cdot CPh_3$
       $Ph \cdot + \cdot CPh_3 \longrightarrow CPh_4$

(B) $Ph \cdot N = N \cdot CPh_3 \longrightarrow \begin{array}{c} Ph \cdots CPh_3 \\ | \quad \quad | \\ N = N \end{array} \longrightarrow Ph \cdot CPh_3 + N_2$

Actually it was found that triphenylmethyl was produced and could be recognised spectroscopically, by colour changes in hot and cold solution and by the formation of the peroxide. The phenyl radicle, presumably formed at the same time, combines with

[56] M. Gomberg and F. W. Sullivan, jun., J. Amer. Chem. Soc., 1922, 44, 1810; A., i, 929.

[57] W. Schlenk and H. Mark, Ber., 1922, 55, [B], 2285, 2299; A., i, 1002.

[58] H. Wieland, E. Popper, and H. Seefried, ibid., 1816; A., i, 772.

hydrogen, but the oxidised component thus necessitated has not yet been recognised. This proves beyond doubt that the azo-compound decomposes with formation of radicles, but it is not logically compulsory to proceed a further step and assume that the tetraphenylmethane formed owes its existence to the operation of scheme A rather than of scheme B. The application of the new method of preparation of triphenylmethyl to the radicles of the basic triphenylmethane dyes is of great interest. It was found, for instance, that phenylazobis-p-dimethylaminotriphenylmethane, $NPh:N\cdot CPh(C_6H_4\cdot NMe_2)_2$, yields on decomposition, benzene, nitrogen, and bis-p-dimethylaminotriphenylmethyl, $CPh(C_6H_4\cdot NMe_2)_2$, which is the radicle of malachite green. This unstable substance and tri-p-dimethylaminotriphenylmethyl, $C(C_6H_4\cdot NMe_2)_3$, the radicle of crystal violet, are scarcely more coloured than triphenylmethyl itself. The observation is interpreted as supporting the quinonoid theory of the structure of the ions of the basic dyestuffs of the triphenylmethane group and it would certainly seem to exclude the Rosenstiehl formula, and Baeyer's ionisable bond modification of this, in a more definite way than has previously been possible. From the point of view of rational classification at least, the papers [59] which Hantzsch has published during the year bearing on the related subjects of the constitution of carbonium salts, halochromism, and solvatochromism, and on the theory of triphenylmethane derivatives contain much that is of value even though, as more than one author claims, many of his suggestions have been anticipated. The lamentable position into which organic chemistry threatens to drift is that there will be as many theoretical systems as theorists, and it is matter for congratulation when several chemists independently arrive at somewhat similar conclusions. It would be impossible to give an adequate exposition of Hantzsch's system in this place, but it may be well to refer to one matter. Only two types of triphenylmethane derivatives are recognised, the colourless non-conducting variety and the coloured conducting, true carbonium compounds in which carbon has normally the co-ordination number 3. Both types are present in the equilibrated system : $Br\cdot CPh_3 \rightleftharpoons$ $[CPh_3]Br$, which may be shifted to the right by the introduction of substances which readily form complex anions with the bromine. But, on the other hand, triphenylmethyl may also function as an anion in such substances as $Na[CPh_3]$, which are also coloured.

This conception of triphenylmethyl as an amphoteric ion leads naturally to the suspicion that the coloured hexa-arylethanes are also complex compounds having the formula $[Ar_3C][Ar_3C]$.

[59] A. Hantzsch, *Ber.*, 1921, **54**, [B], 2573, 2613, 2620, 2627; 1922, **55**, [B], 953; *A.*, i, 24—26, 556. Compare also *A.*, i, 331, 445.

Carbinols containing phenylethinyl groups have been prepared and found to exhibit typical halochromism.[60] For example, triphenylethinylcarbinol, $(CPh\!:\!C)_3C\!\cdot\!OH$, is obtained by the action of magnesium phenylethinyl bromide on phenylpropiolyl chloride. It gives a bluish-violet coloration with sulphuric acid, deep bluish-violet with perchloric acid, and bright blue with stannic chloride. The conclusion drawn is that the halochromy of triphenylcarbinols is not to be associated with changes in the benzene rings, since the typical phenomena can be reproduced when " gap linkings " are introduced between the carbinol group and the nuclei. A number of distinct investigations published during the year bear on the same subject.[61] Diphenylphenylethinylcarbinol is converted by acetyl chloride, acetic anhydride, and the like and by hydrogen chloride in ethereal solution into phenyl α-phenylstyryl ketone : [62] $CPh\!:\!C\!\cdot\!CPh_2\!\cdot\!OH \longrightarrow COPh\!\cdot\!CH\!:\!CPh_2$. That the arrangement of carbon atoms remains undisturbed (wandering of phenyl was a possibility) was proved by carrying out the transformation : $CPh\!:\!C\!\cdot\!C(C_6H_4Cl)_2\!\cdot\!OH \longrightarrow COPh\!\cdot\!CH\!:\!C(C_6H_4Cl)_2$ and oxidising the product to pp'-dichlorobenzophenone. The puzzling feature of the reaction is that it occurs so readily in the absence of water. It may be mentioned here that the fate of over-oxidised leuco-bases of the triphenylmethane dyestuffs has been ascertained. The gradual treatment at the ordinary temperature of a moderately concentrated malachite-green solution, acidified with sulphuric acid, with lead peroxide until a diluted sample shows no green tinge, followed by filtration and addition of perchloric acid, precipitates orange needles of tetramethyldiphenoquinoneimonium perchlorate,

$$ClO_4\left\{NMe_2\!\!=\!\!\left\langle\underset{=}{=}\right\rangle\!\!=\!\!\left\langle\underset{=}{=}\right\rangle\!\!=\!\!NMe_2\right\}ClO_4. \quad {}^{(63)}$$

The same perchlorate results from the oxidation of tetramethyl-benzidine or of Michler's hydrol.

Alicyclic Group.

There is much overlapping of the subject matter of the sections of this report and numerous references to alicyclic compounds will be found elsewhere. A synthesis of 1-methyl*cyclo*propane-1-carboxylic acid (I) has been carried through the following

[60] K. Hess and W. Weltzien, *Ber.*, 1921, **54**, [*B*], 2511; *A.*, i, 35.

[61] F. Straus and A. Dützmann, *J. pr. Chem.*, 1921, [ii], **103**, 1; *A.*, i, 148; K. Ziegler, *Ber.*, 1921, **54**, [*B*], 3003; *A.*, i, 151; S. Skraup and L. Freundlich, *ibid.*, 1922, **55**, [*B*], 1073; *A.*, i, 539; K. H. Meyer and K. Schuster, *ibid.*, 815; *A.*, i, 540.

[62] *Ibid.*, 819; *A.*, i, 556.

[63] F. Kehrmann, G. Roy, and (Miss) M. Ramm, *Helv. Chim. Acta*, 1922, **5, 153**; *A.*, i, 467.

stages : [64] Formaldehyde (2 mols.) and propaldehyde (1 mol.) are condensed to dihydroxy-$\alpha\alpha$-dimethylpropaldehyde, $CHO \cdot CMe(CH_2 \cdot OH)_2$, which is converted into its *oxime* and then by the action of acetic anhydride into diacetoxypivalonitrile. The latter, by heating with saturated hydrobromic acid at 125—130° during twenty hours, yields dibromopivalic acid, $CMe(CH_2Br)_2 \cdot CO_2H$. Methyl dibromopivalate reacts with zinc dust in methyl alcoholic solution with formation of methyl 1-methyl*cyclo*propane-1-carboxylate.

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \!\!> \!\! CMe \cdot CO_2H \qquad \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \!\!> \!\! CH \cdot CH\!:\!CH_2 \qquad \begin{matrix} CH_2 \cdot C\!:\!CH_2 \\ | \quad | \\ CH_2 \cdot CH_2 \end{matrix}$$

(I.)   (II.)   (III.)

The isomeric hydrocarbons vinyl*cyclo*propane (II) and methylene*cyclo*butane (III) have each been produced by the decomposition of suitable quaternary ammonium compounds.[65] Acetyl*cyclo*propane-oxime, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!> \!\! CH \cdot CMe\!:\!NOH$, is reduced to the amine, which is fully methylated and the iodide converted to hydroxide. The distillation of this trimethyl-α-*cyclo*propylethylammonium hydroxide, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!> \!\! CH \cdot CHMe \cdot NMe_3 \!\Big\} OH$, furnishes chiefly vinyl*cyclo*propane and very little of the tertiary base. Methylene*cyclo*butane is similarly prepared in small yield from *cyclo*butylmethyltrimethylammonium hydroxide, $CH_2 \!<\!\! \begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!> \!\! CH \cdot CH_2 \cdot NMe_3 \!\Big\} OH$, which, however, gives on decomposition *cyclo*butylmethyldimethylamine as the main product. The action of hypochlorous acid on methylene*cyclo*butane gives rise to a chlorohydrin,

$$CH_2 \!<\!\! \begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!> \!\! C(OH) \cdot CH_2Cl \quad \text{or} \quad CH_2 \!<\!\! \begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!> \!\! CCl \cdot CH_2 \cdot OH,$$

the former being indicated by analogies. This is converted into *cyclo*pentanone when it is heated with litharge and water, whilst the action of aqueous potassium hydroxide produces an oxide, $CH_2 \!<\!\! \begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!> \!\! C \!<\!\! \begin{matrix} CH_2 \\ O \end{matrix}$, which may be isomerised to *cyclo*butane-aldehyde, $CH_2 \!<\!\! \begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!> \!\! CH \cdot CHO$, by the action of zinc chloride.[66]

When campholenic acid (IV) is treated with an aqueous solution of calcium hydroxide and with silver oxide at 60°, it is partly reduced to camphor and partly oxidised to α-ketocampholenic acid (V).[67]

[64] M. Kohn and A. Mendelewitsch, *Monatsh.*, 1921, **42**, 227; *A.*, i, 518.

[65] N. J. Demjanov and (Miss) M. Dojarenko, *Ber.*, 1922, **55**, [*B*], 2718, 2727; *A.*, i, 1014, 996.

[66] *Ibid.*, 2730; *A.*, i, 1009.

[67] J. P. C. Chandrasena and C. K. Ingold, *T.*, 1922, **121**, 1552.

E* 2

$$CH\!:\!CMe \quad >CMe_2 \quad CH_2\!\cdot\!CH\!\cdot\!CH_2\!\cdot\!CO_2H$$
(IV.)

$$CH\!:\!CMe \quad >CMe_2 \quad CH_2\!\cdot\!CH\!\cdot\!CO\!\cdot\!CO_2H$$
(V.)

$$CH_2\!\cdot\!CHMe \quad >CMe_2 \quad CH_2\!\cdot\!CH\!\cdot\!CH_2\!\cdot\!CO_2H$$
(VI.)

The yield of camphor obtained is stated to be small, but is not precisely specified, so that it is difficult to form an independent opinion as to the significance of this very striking observation. If the view put forward, that *trans*-dihydrocampholenic acid (VI) is the intermediate stage, is correct, then we have another and a peculiar instance of the abnormal reactivity of a newly formed molecule, because both *cis*- and *trans*-dihydrocampholenic acids have been isolated by another investigator in their racemic forms and found to be perfectly stable substances.[68] The condensation of chloral with methyl malonate leads to the formation of methyl $0:3:3$-*dicyclo*-Δ^1-octene-$3:7$-dione-$2:4:6:8$-tetracarboxylate (VII), which can be converted by hydrolysis and reduction into the diketone (VIII), the glycol (IX), and finally into $0:3:3$-*dicyclo*-octane (X).[69]

$$CO\!<\!\!\genfrac{}{}{0pt}{}{C(CO_2Me)\!=\!C-CH(CO_2Me)}{CH(CO_2Me)\cdot CH\cdot CH(CO_2Me)}\!\!>\!CO$$
(VII.)

$$CO\!<\!\!\genfrac{}{}{0pt}{}{CH_2\cdot CH\cdot CH_2}{CH_2\cdot CH\cdot CH_2}\!\!>\!CO$$
(VIII.)

$$HO\cdot CH\!<\!\!\genfrac{}{}{0pt}{}{CH_2\cdot CH\cdot CH_2}{CH_2\cdot CH\cdot CH_2}\!\!>\!CH\cdot OH$$
(IX.)

$$CH_2\!<\!\!\genfrac{}{}{0pt}{}{CH_2\cdot CH\cdot CH_2}{CH_2\cdot CH\cdot CH_2}\!\!>\!CH_2$$
(X.)

Tautomerism.

1 : 5-Dihydroxynaphthalene reacts with sodium hydrogen sulphite to produce a compound, $C_{10}H_{10}O_8S_2Na_2$, which, on boiling with water, loses one molecular proportion of sodium hydrogen sulphite and is changed to sodium 5-hydroxy-1-ketotetrahydro-naphthalene-3-sulphonate (I). 2 : 7-Dihydroxynaphthalene behaves somewhat differently and gives the compound II, which is converted by dry ammonia at 100° into a corresponding amino-derivative (III). The latter on decomposition with water yields 7-amino-2-naphthol.[70]

$$(I.) \quad HO\cdot C_6H_3\!<\!\!\genfrac{}{}{0pt}{}{CO-CH_2}{CH_2\cdot CH\cdot SO_3Na}$$

$$HO\cdot C_6H_3\!<\!\!\genfrac{}{}{0pt}{}{CH_2\cdot C(OH)\cdot SO_3Na}{CH\!=\!CH} \quad (II.)$$

$$HO\cdot C_6H_3\!<\!\!\genfrac{}{}{0pt}{}{CH_2\cdot C(NH_2)\cdot SO_3Na}{CH\!=\!CH} \quad (III.)$$

[68] P. Lipp, *Ber.*, 1922, **55**, [*B*], 1883; *A.*, i, 735.

[69] G. Schroeter and G. Vossen, *Annalen*, 1922, **426**, 1; *A.*, i, 122.

[70] W. Fuchs and W. Stix, *Ber.*, 1922, **55**, [*B*], 658; *A.*, i, 451.

The series of reactions throws light on the mechanism of Bucherer's process for the conversion of naphthols into naphthylamines, but it is surprising that it should also be claimed as a demonstration of the tautomerism of the dihydroxynaphthalenes. It has long been thought that the α-diketones may exist in a peroxide form, and Willstätter's discovery of colourless and coloured modifications of o-benzoquinone was interpreted in this way. Definite confirmation of the accuracy of the hypothesis is now provided by a careful investigation of the benzils.[71] Normally, these compounds are, of course, yellow, but in certain cases they have been found to be colourless or almost so. The first example was discovered by J. C. Irvine in 1907 when he prepared the colourless 2 : 2'-dimethoxy-benzil.[72] The coloured benzils react readily with o-phenylenedi-amine with formation of quinoxalines and are readily oxidised by hydrogen peroxide to two molecules of substituted benzoic acids. The observation has now been made that the colourless benzils exhibit neither of these reactions with facility. The colourless compounds often give pale yellow solutions, and this suggests the existence of an equilibrium :

$$\text{R·CO·CO·R} \rightleftharpoons \begin{array}{c} \text{R·C}=\text{C·R} \\ \text{O}-\text{O} \end{array}$$

Yellow.   *Colourless.*

It is in fact found that the reactivity of a benzil is roughly proportional to the intensity of colour of its solution. Finally, in 4 : 4'-dibenzyloxybenzil, $CH_2Ph·O·C_6H_4·CO·CO·C_6H_4·O·CH_2Ph$ (IV), a substance has been discovered which can be isolated in bright yellow diketonic and colourless peroxidic forms.

The latter is obtained by quickly cooling a concentrated ethereal solution of the substance. It crystallises in colourless needles which become yellow at 121° and melt indefinitely at 124°. This is the labile modification and if allowed to remain in contact with the solvent passes into solution, whilst yellow prisms of the more stable diketonic form, melting sharply at 126°, grow at its expense. The two substances are distinguished by their differing behaviour with reagents in the sense already indicated, so that this is a true case of tautomerism involving two chemical individuals which are in equilibrium in solution. Both yellow and colourless forms are unimolecular in solution and this is also true of benzils which exist

[71] A. Schönberg and O. Kraemer, *Ber.*, 1922, **55**, [B], 1174; *A.*, i, 663; A. Schönberg and W. Bleyberg, *ibid.*, 3753.

[72] *T.*, 1907, **91**, 541. The substance first saw the light, which it refused to absorb, in the chemical laboratories of the University of Leipzig. The comment of Wislicenus, " *Das ist kein benzil*," does not appear to have been far from the mark.

exclusively in yellow or colourless modifications respectively. Thus 2 : 2'-diethoxybenzil is unimolecular in its colourless solutions. The phenomenon is accordingly not at all analogous to the polymerisation of coloured nitroso-compounds to colourless dimerides. One consequence of this work and that of Willstätter is to dispose of the idea that the colour of the α-diketones and of the quinones is due to oscillations between diketonic and peroxidic forms. In solutions in which equilibrium is established the colour is of feeble intensity on account of the lower concentration of the coloured modification. Another new type of tautomerism (ring-chain), which can be followed by a colour change due to the production of an α-diketonic group, is exhibited by the remarkable compound having the constitution VI.

(V.)
$$\text{CH}_2 \quad \text{CMe·CH}_2\text{·CO}_2\text{H} \quad \text{CO} \quad \text{CO}$$
Yellow.

(VI.)
$$\text{CH}_2 \quad \text{CMe·CH}_2\text{·CO} \quad \text{C(OH)—O} \quad \text{CO}$$
Colourless.

The substance clearly fulfils the requirements of true tautomerism and can be converted into derivatives from the diketonic form (V) or from the lactonic form (VI). With o-phenylenediamine, it yields a quinoxaline, and oxidises as a diketone when treated with hydrogen peroxide. On the other hand, acetylation produces the acetyl derivative of the keto-lactone. The colourless solution in water becomes yellow on heating and colourless again on cooling and it is important to notice that the same change occurs in neutral solvents, although more slowly.[73] In alkaline solution there is evidence of ring-chain tautomerism of another kind, but this is best discussed in connexion with a different example which has the added interest that the occurrence of the phenomenon was anticipated as the result of theoretical considerations.[74]

The ordinary keto-enol isomeric change may be regarded as a reversible aldol-type condensation involving a carbonyl group and the methylene group, activated by itself, often, however, assisted in the latter function by other groups such as the carbethoxyl in ethyl acetoacetate. In suitably constituted substances, the carbonyl and methylene groups might be separated by a chain of atoms, and the object of the work now under discussion was to find such a case in which the separation is by one carbon atom. In other words, to realise the equilibrium :

$$>\text{C}<\genfrac{}{}{0pt}{}{\dot{\text{C}}\text{O}}{\text{CH}_2} \;\rightleftharpoons\; >\text{C}<\genfrac{}{}{0pt}{}{\dot{\text{C}}\text{(OH)}}{\text{CH}} \;.$$

[73] G. A. R. Kon, A. Stevenson, and J. F. Thorpe, *T.*, 1922, **121**, 650.
[74] S. S. Deshapande and J. F. Thorpe, *ibid.*, 1430.

The series chosen for investigation was that of the α-ketoglutaric acids, and earlier work had shown that α-keto-ββ-dimethylglutaric acid exists in the open-chain form (VII), whilst the related *cyclo*-hexane derivative prefers the hydroxy-ring arrangement (VIII).

(VII.) $Me_2C<^{CO·CO_2H}_{CH_2·CO_2H}$ $C_5H_{10}>C<^{C(OH)·CO_2H}_{CH_2·CO_2H}$ (VIII.)

This was explained in terms of a hypothesis relating to the effect of attached groups on the carbon tetrahedral angle. The two methyl groups in VII do not bring the methylene and carbonyl groups into sufficiently close proximity, whilst the effect of the *cyclo*hexane ring in VIII is to cause them to approach so close to one another that the *cyclo*propane ring is readily formed and also stable. In order to realise tautomerism it was desirable to find substituting groups in the β-positions which would have an effect greater than that of *gem*-dimethyl and less than that of penta-methylene. Theoretically, this should be found in the *gem*-diethyl group, and α-keto-ββ-diethylglutaric acid (IX) was accordingly prepared by the action of very concentrated, hot aqueous potassium hydroxide on ethyl αα'-dibromo-ββ-diethylglutarate (XI). The conditions can be so adjusted that either the acid (IX) or the hydroxy-ring acid (X) constitutes the main product, and the two substances can be separated by means of ether, which dissolves the former only.

$Et_2C<^{CO·CO_2H}_{CH_2·CO_2H}$ $Et_2C<^{C(OH)·CO_2H}_{CH·CO_2H}$ $Et_2C<^{CHBr·CO_2Et}_{CHBr·CO_2Et}$

(IX.)   (X.)   (XI.)

These compounds are not themselves tautomerides, but a tautomeric equilibrium of their salts is set up in a concentrated solution of potassium hydroxide (64 per cent.). The equilibrium mixture reached from either side contains approximately 38 per cent. of the keto-form. The tendency of this series of researches is to show that tautomerism of the ring-chain type may be anticipated as the result of reversible intramolecular additions analogous to all known intermolecular reversible additive reactions capable of joining two chains. Stereochemical considerations, and those connected with reactivity in general, are introduced in order to arrive at suitable test cases. Just as the keto-enol change is the simplest example of the reversible addition of —CH_2 to —C=O, so the glutaconic acid, three-carbon tautomerism is the simplest known case of reversible addition of —CH_2— to —C=C. Now the best known reversible intermolecular reaction of the latter kind is the Michael condensation, and an exhaustive investigation [75] has

[75] C. K. Ingold, E. A. Perren, and J. F. Thorpe, *T.*, 1922, **121**, 1765.

brought to light several examples of ring-chain tautomerism in which the equilibrium set up is strictly analogous to that resulting when sodiomalonic ester is allowed to react with an αβ-unsaturated ester.[76] A summary of the whole of the work on this subject cannot even be attempted, but an isolated example may be mentioned. The action of piperidine on ethyl dicarboxygluta-conate (XII) [77] leads to the formation of the esters XIII and XIV in successive stages, and the process is reversed by sodium ethoxide.

$$(CO_2Et)_2CH \cdot CH\!:\!C(CO_2Et)_2$$

(XII.)

$$(CO_2Et)_2\overset{|}{C} \cdot CH\!:\!C(CO_2Et)_2$$
$$(CO_2Et)_2CH \cdot \overset{|}{C}H \cdot CH(CO_2Et)_2$$

(XIII.)

(XIV.) $$(CO_2Et)_2CH \cdot \overset{|}{C}H \cdot \overset{|}{C}(CO_2Et)_2$$
$$(CO_2Et)_2\overset{|}{C}\!\!-\!\!\overset{|}{C}H \cdot CH(CO_2Et)_2$$

The individuals XIII and XIV can be separated and isolated, the former being a liquid and the latter a solid, melting at 103°. The two substances have, however, been shown to be in tautomeric equilibrium in a solvent or at slightly higher than normal temperatures so as to avoid the disturbance produced by crystallisation. The mixture contains about 80 per cent. of the cyclic ester (XIV) and the attainment of equilibrium is much facilitated by the addition of piperidine, although not absolutely dependent on this. Although the isomeric changes involved are far more sluggish than those with which we are familiar in the case of ethyl acetoacetate, the claim is justified that the term tautomerism is equally applicable to both examples. When ring-chain tautomerism involves the production of a bridge in a substance already cyclic, it is called intra-annular tautomerism and the distinction is not only convenient but also desirable from the point of view that what may be called the chemical potential of the groups involved need not be so great as in ring-chain tautomerism owing to the close space relationship of some of the constituent atoms of a ring. It has already been shown that the acid XV behaves in some of its reactions as if it had the formula XVI.[78]

(XV.) $$Me_2C\!\!<\!\!\begin{array}{l}C(CO_2H) \cdot \overset{|}{C}H \cdot CO_2H\\ \overset{|}{C}H\!\!-\!\!-\!\!-\!\!CO\end{array}$$ $$Me_2C\!\!<\!\!\begin{array}{l}C(CO_2H)\!:\!\overset{|}{C} \cdot CO_2H\\ CH_2\!\!-\!\!-\!\!-\!\!\overset{|}{C}O\end{array}$$ (XVI.)

An even more complete investigation of the decarboxylated acid (XVII) has now been carried out with results which demonstrate the existence of the indicated equilibrium.[79] The question of the formula to be assigned to the solid acid has not yet been answered.

[76] C. K. Ingold and E. A. Perren, *T.*, 1922, **121**, 1582; C. K. Ingold and W. J. Powell, *ibid.*, 1796.

[77] Guthzeit, *Ber.*, 1901, **34**, 675; Guthzeit, Weiss, and Schafer, *J. pr. Chem.*, 1909, [ii], **80**, 412.

[78] E. H. Farmer and C. K. Ingold, *T.*, 1920, **117**, 1362.

[79] E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *ibid.*, 1922, **121**, 128.

The following relations illustrate a part of the proof of the separate existence of the isomerides which is offered.

$$CMe_2 \begin{cases} CO_2H \\ C\!:\!CH\!\cdot\!CO_2H \\ CO_2H \end{cases}$$

$$CMe_2 \begin{cases} CO_2H \\ C\!=\!CH \\ CH_2\!\cdot\!CO \end{cases} \quad \rightleftharpoons \quad CMe_2 \begin{cases} CO_2H \\ C\!-\!CH_2\!\cdot\! \\ CH\!\cdot\!CO \end{cases}$$

(XVII.)

$$CMe_2 \begin{cases} C(OH)_2\!\cdot\!CO_2H \\ CH_2\!\cdot\!CO_2H \end{cases}$$

$$CMe_2 \begin{cases} CO_2H \\ C\!=\!CH \\ CO\!\cdot\!CO \end{cases}$$

$$CMe_2 \begin{cases} CO_2H \\ C\!\cdot\!CH \\ C\!\cdot\!CO \\ NOH \end{cases}$$

$$CMe_2 \begin{cases} C(OH)\!:\!C\!\cdot\!Cl \\ CH_2\!-\!\cdot\!CO \end{cases}$$

$$CMe_2 \begin{cases} CO\!-\!CCl_2 \\ CH_2\!\cdot\!CO \end{cases}$$

$$CMe_2 \begin{cases} C(CO_2H)\!\cdot\!CCl_2 \\ CCl\!-\!\!\!-\!CO \end{cases}$$

$$CMe_2 \begin{cases} C(CO_2H)_2 \\ CH\!\cdot\!CO_2H \end{cases}$$

$$CMe_2 \begin{cases} CH\!\cdot\!CO_2H \\ CH\!\cdot\!CO_2H \end{cases}$$

K,Fe(CN).   KMnO.   NOCl   HCl   CH₂O   H₂O₂   alkali

This again is a perfectly clear case in which the reaction involved is analogous to the Michael condensation, being an addition of $-CH_2-$, α- to carbonyl, to an αβ-unsaturated ketone. Analogies are not, however, so readily found for another case of intra-annular tautomerism which is now suspected to occur in the well-known substance, α-campholytic acid (XVIII).[80]

$$\text{(XVIII.)} \quad CMe_2 {<}^{CMe\overline{\quad\quad}CH}_{CH(CO_2H)\cdot CH_2} \rightleftharpoons CMe_2 {<}^{CMe\overline{\quad\quad}CH_2}_{C(CO_2H)\cdot CH_2}$$

The discussion of the evidence, which is based on a study of the oxidation of the acid under various conditions, involves a closely reasoned and somewhat complex argument which does not lend itself to summarisation. The following are some of the points. Alkaline permanganate oxidises α-campholytic acid to the glycol XIX and the keto-dibasic acid XX and this is consistent with the double-bonded formula only. ·

$$\text{(XIX.)} \quad CMe_2 {<}^{CMe(OH)-CH\cdot OH}_{CH(CO_2H)\cdot CH_2} \qquad CMe_2 {<}^{COMe \quad\;\; CO_2H}_{CH(CO_2H)\cdot CH_2} \quad \text{(XX.)}$$

On the other hand, acidified chlorate and osmium tetroxide in the cold produces several products, among which are found the tautomeric substance often called Balbiano's acid (XXI) and a lactonic acid of the formula XXII.

$$CMe_2 {<}^{CMe\cdot CO_2H}_{C(OH)\cdot CO_2H} \rightleftharpoons CMe_2 {<}^{CHMe\cdot CO_2H}_{CO\cdot CO_2H} \qquad CMe_2 {<}^{CHMe\cdot CO}_{CH\cdot CO_2H}^{\quad O}$$
$$\text{(XXI.)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(XXII.)}$$

The latter substance was compared with a specimen synthetically prepared. These and other results are regarded as proving that α-campholytic acid also exists in the bridged-ring form and that the substance exhibits intra-annular tautomerism. It is certainly difficult to imagine a different interpretation of the results, but the proof is not quite so conclusive as in some of the other new cases of tautomerism, because it depends wholly on the course of degradations which *might* involve some obscure transformation.

Ring Formation.

The value of the theory connecting the angles between carbon-to-carbon valencies and the atomic volumes of the attached groups is confirmed in a general way by the correspondence between the anticipated order of sequence in a series of substances and the facts observed in relation to such properties as the ease of formation

[80] J. P. C. Chandrasena, C. K. Ingold, and J. F. Thorpe, *T.*, 1922, **121**, 1542.

of cyclic compounds. In the three compounds glutaric acid, β-methylglutaric acid, and ββ-dimethylglutaric acid, the calculated angles are as indicated and it has been shown that the ease of formation of the *cyclo*propane ring, by connecting the carbon atoms in the α-positions, increases as this angle diminishes.

$$CH_2\underset{\diagdown CH_2 \cdot CO_2H}{\overset{\diagup CH_2 \cdot CO_2H}{\langle\textit{115·3°}}} \qquad MeCH\underset{\diagdown CH_2 \cdot CO_2H}{\overset{\diagup CH_2 \cdot CO_2H}{\langle\textit{112·5°}}} \qquad Me_2C\underset{\diagdown CH_2 \cdot CO_2H}{\overset{\diagup CH_2 \cdot CO_2H}{\langle\textit{109·5°}}}$$

The method adopted was similar to that used previously and consisted in estimating as far as possible all the products formed by the treatment of the esters of the α-bromo-acids with alkali under standard conditions. In the following table, taken from the original,[81] the new data are those for the β-methylglutaric acid series and it should be noted that the amount of *cyclo*propane acids quoted includes the products which can only have been derived by subsequent decomposition of these substances.

	Derivatives from		
Products.	glutaric acid per cent.	β-methyl- glutaric acid per cent.	ββ-dimethyl- glutaric acid per cent.
α-Hydroxyglutaric acids	16	8	4
Glutaconic acids	3	9	0
*cyclo*Propane acids	47	64	84
	66	81	88

These results are in excellent agreement with the theory and it should be remarked that non-steric effects are to a large extent eliminated by the method chosen, which is to compare the extent of ring formation with the extent of occurrence of a side reaction, in this case hydroxylation. It is a reasonable assumption that changes in the reactivity of the bromine would be approximately equally effective in stimulating and retarding both reactions. Such results are not related, however, to the precise angles quoted in any way except by the placing of a series in a certain order. Compounds of the type $RR'C\underset{\diagdown C(CN)\cdot CO}{\overset{\diagup C(CN)\cdot CO}{\langle}}NH$ have been prepared in order to compare the effects of the substituents R,R' on the stability of the *cyclo*propane ring.[82] Previous work had shown that when R and R' are methyl, the hydrolysis of the complex gives an open-chain hydroxy-acid (lactone), whilst, under similar conditions, the three-carbon ring remains intact when CRR' is *cyclo*hexylene. But this characteristic stability is destroyed by the substitution of a methyl group in positions 3 or 4 in the *cyclo*hexane ring; a very

[81] C. K. Ingold, *T.*, 1922, **121**, 2676.
[82] S. F. Birch and J. F. Thorpe, *ibid.*, 1821.

remarkable result which would seem to imply a steric effect at a distance, possibly having some connexion with the varieties of buckling, of which the *cyclo*hexane ring appears to be capable. In relation to this subject it may be noted that *cis-* and *trans-cyclo*-hexane-1 : 2-dicarboxylic acids both form inner anhydrides, of which the former is the more stable and is produced from the *trans*-anhydride on heating.[83]

It has frequently been observed that ease of formation and stability of cyclic systems are not necessarily parallel and the *cyclo*butane series furnishes some of the best examples. Thus *cyclo*butanone, hitherto a very inaccessible compound, may be obtained in a yield of 15 per cent. by the pyrogenic decomposition of 1-hydroxy*cyclo*butane-1-carboxylic acid and is consequently a very stable substance.[84]

$$CH_2{<}{{CH_2}\atop{CH_2}}{>}C(OH){\cdot}CO_2H \dashrightarrow CH_2{<}{{CH_2}\atop{CH_2}}{>}CO + CO + H_2O.$$

In contrast, *cyclo*butanone derivatives can only be prepared by the aid of the Dieckmann reaction in exceptionally favourable cases and then only in very poor yields. Ethyl *cyclo*hexane-1 : 1-diacetate (I) reacts with potassium in xylene solution with formation of a mixture of products from which *cyclo*hexane*spirocyclo*butanone (II) and *cyclo*hexane*spirocyclo*pentane-3 : 4-dione (III) can be isolated.[85]

$$CH_2{<}{{CH_2{\cdot}CH_2}\atop{CH_2{\cdot}CH_2}}{>}C{<}{{CH_2{\cdot}CO_2Et}\atop{CH_2{\cdot}CO_2Et}} \qquad CH_2{<}{{CH_2{\cdot}CH_2}\atop{CH_2{\cdot}CH_2}}{>}C{<}{{CH_2}\atop{CH_2}}{>}CO$$

(I.) (II.)

$$CH_2{<}{{CH_2{\cdot}CH_2}\atop{CH_2{\cdot}CH_2}}{>}C{<}{{CH_2{\cdot}CO}\atop{CH_2{\cdot}CO}}$$

(III.)

The *cyclo*butanone derivative is a stable saturated ketone, which is unfortunately obtained in a yield amounting to little more than 1 per cent. Its formation is an indication that the Dieckmann reaction occurs, but does not prove this, as the ketone might have been derived from III by a degradation similar to that which phenanthraquinone suffers in its change to fluorenone. The suggested mechanism of formation of the diketone III is the following :

$$R{<}{{CH_2{\cdot}CO_2Et}\atop{CH_2{\cdot}CO_2Et}} \rightarrow R{-}{{CH{\cdot}CO_2Et}\atop{CH_2{\cdot}CO}} \xrightarrow{2H} R{<}{{CH_2{\cdot}CO{\cdot}OEt}\atop{CH_2{\cdot}CHO}} \rightarrow R{<}{{CH_2{\cdot}CO}\atop{CH_2{\cdot}CO}}$$

[83] A. Windaus and W. Hückel, *Nachr. Ges. Wiss. Göttingen, Math. physic. Klasse*, 1920, **11**, ii, 181; *A.*, i, 658.

[84] W. J. Demjanov and (Miss) M. Dojarenko, *Ber.*, 1922, **55**, [*B*], 2737; *A.*, i, 1161.

[85] G. A. R. Kon, *T.*, 1922, **121**, 520.

It seems simpler to regard it as a pinacol-like reduction of the carbethoxyl groups thus : $-CO_2Et + K \rightarrow \overset{|}{C}(OK)\cdot OEt$; $2\overset{|}{C}(OK)\cdot OEt \rightarrow -CO\cdot CO- + 2KOEt$. The diketone may then be reduced to a keto-alcohol, and this view is supported by the fact that ethyl diethoxyacetate reacts with potassium with formation of the ketonic alcohol, $(EtO)_2CH\cdot CO\cdot CH(OH)\cdot CH(OEt)_2$.[86]

A systematic investigation of the application of the Dieckmann reaction to the preparation of benzoketopolymethylenes has been commenced by a study of one of the more favourable cases. The action of sodium at 100° on a toluene solution of ethyl o-phenylenediacetate (IV) causes the separation of the sodium derivative of ethyl 2-hydrindone-1-carboxylate (V) in a yield of 90 per cent. of that theoretically possible.[87]

(IV.) — CH₂·CO₂Et / CH₂·CO₂Et   (V.) — CH₂ / CO / CH·CO₂Et

Natural Products.

The terpene present in the essential oil from *Andropogon Jwarancusa*, Jones, appears to be Δ^4-carene (I). This conclusion is based on the following facts.[88] The hydrocarbon is dicyclic, as it forms a dibromide and a monohydrochloride in ethereal solution. In acetic acid solution, it forms a dihydrochloride, identified as dipentene dihydrochloride, and in addition an oily dihydrochloride, probably that of sylvestrene, because the regenerated terpene gives the highly specific reaction with acetic anhydride and sulphuric acid. This indicates very clearly a hydrocarbon of the carene group. In contradistinction from the Δ^3-carene (II), which has been proved to occur in the oil of *Pinus longifolia*,[89] the molecular refraction showed considerable exaltation, which is in agreement with the suggested formula.

(I.)   (II.)   (III.)

[86] A. Wohl and B. Mylo, *Ber.*, 1912, **45**, 322.
[87] W. H. Perkin and A. F. Titley, *T.*, 1922, **121**, 1562.
[88] J. L. Simonsen, *ibid.*, 2292.
[89] *Ibid.*, 1920, **117**, 570.

The results of permanganate oxidation are consistent with the carene structure, since the main product is an optically active acid isomeric with pinonic acid. It probably has the constitution III and is changed by hypobromite into bromoform and an isomeride of pinic acid. The ease with which the ring may be opened is an argument in favour of the *cyclo*propane formula. It is remarkable that two members of the carene group, which had not previously been found to occur in nature, should have been isolated by one investigator during such a short period of time. A substantial accretion to our knowledge of the sesquiterpenes has resulted from an investigation of the nature of the aromatic compounds which are produced from them by heating with sulphur.[90] Dehydrogenation in this way converts cadinene, tetrahydrocadinene, calamenol, calamene, calamenene, zingiberene, *iso*zingiberene, and the sesquiterpene from Javanese citronella oil into one and the same hydrocarbon, $C_{15}H_{18}$, termed cadalene. This is clearly a naphthalene derivative and on the assumption that the relation of the open-chain alcohol, farnesol, to cadinene is analogous to that of a typical olefine terpene alcohol of the C_{10}-group to a *p*-cymenoid terpene, the guess was made that cadalene should be 1 : 6-dimethyl-4-*iso*-propylnaphthalene (IV). A synthesis of the latter hydrocarbon was carried out and the substance was found to be identical with cadalene. The later stages are indicated below :

Very valuable information regarding the carbon skeleton of some sesquiterpenes is thus obtained, but the reservation is made that since zingiberene is monocyclic it is evident that the naphthalene ring is to be regarded as only potentially present in the molecule. When eudesmol and selinene are heated with sulphur, a hydrocarbon, $C_{14}H_{14}$, called eudalene, is produced. This also is a naphthalene derivative and its production is supposed to be due to the occurrence in the parent molecule of a methyl group which cannot

[90] L. Ruzicka, J. Meyer, and M. Mingazinni, *Helv. Chim. Acta*, 1922, 5, 345; *A.*, i, 560; L. Ruzicka and C. F. Seidel, *ibid.*, 369; *A.*, i, 562; L. Ruzicka and M. Mingazzini, *ibid.*, 710; *A.*, i, 1001.

survive the transition into an aromatic compound. A similar case is the production of retene from abietic acid. Cadalene (IV) on oxidation with chromic acid yields a naphthoic acid, $C_{15}H_{16}O_2$, which must have the constitution V because it can be converted to a methyl*iso*propylnaphthalene (VI) which is not identical with the synthesised 1-methyl-4-*iso*propylnaphthalene (VII).

CO₂H structures:

CO_2H / Me (V.)

Pr^β / Me (VI.)

Me / Pr^β (VII.)

(V.) (VI.) (VII.)

Neither VI nor VII is identical with eudalene, which is therefore not an *apo*cadalene as was at first supposed. Ruzicka and his collaborators have also attacked the problem of the constitution of abietic acid, but the discussion of the results as well as of those of Windaus and his co-workers on cholesterol, the bile-acids, and allied subjects must be deferred. It is not too optimistic to hope that a little more information will enable the final elucidation of these problems to be chronicled.

The main constituent of Japanese lac is a mixture, called urushiol, containing 10 per cent. of hydrourushiol, into which all the other constituents are converted by reduction. Hydrourushiol has already been shown to be 2 : 3-dihydroxy-*n*-pentadecylbenzene (VIII).

(VIII.) OH / OH / $C_{15}H_{31}$

(IX.) OH / OH / $-[CH_2]_9 \cdot CH:CH \cdot [CH_2]_5 \cdot CH_3$

The products of the action of ozone on urushiol diacetate and dimethyl ether are such as can be explained by the supposition that urushiol contains the compounds

$$C_6H_3(OH)_2 \cdot [CH_2]_7 \cdot CH:CH \cdot [CH_2]_5 \cdot CH_3$$

and $C_6H_3(OH)_2 \cdot [CH_2]_7 \cdot CH:CH \cdot [CH_2]_4 \cdot CH:CH_2$.[91] The main constituent of Indo-Chinese lac called " laccol " has the constitution IX.[92] Its dimethyl ether yields a mono-ozonide which is decomposed by boiling water with formation of heptaldehyde, nonane-$\omega\omega'$-dicarboxylic acid, and an aldehyde of the composition $C_6H_3(OMe)_2 \cdot [CH_2]_9 \cdot CHO$. The simultaneous formation of acetaldehyde and formic acid as well as of more complex fatty-aromatic aldehydes indicates the occurrence of constituents of laccol other than IX, but these are probably all closely related. Hydrolaccol dimethyl ether forms a mononitro- and a dinitro-derivative and the latter fact suffices to prove that the substance cannot be a 4-sub-

[91] R. Majima, *Ber.*, 1922, **55**, [*B*], 172; *A.*, i, 262.
[92] *Ibid.*, 191; *A.*, i, 263.

stituted veratrole. The outcome of the attempt to dinitrate 4-alkylveratroles is invariably to produce 4 : 5-dinitroveratrole as the result of displacement.

Burmese lac contains " thitsiol " reducible to hydrothitsiol, which is shown to be 4-n-heptadecylcatechol (X) by direct synthesis. Margaric acid is condensed with catechol in presence of stannic chloride, and the 3 : 4-dihydroxyphenyl heptadecyl ketone is then reduced by means of amalgamated zinc and hydrochloric acid (Clemmensen).

(X.) HO —[CH_2]$_{16}$·CH_3 MeO $C_{17}H_{35}$ (XI.)
HO MeO NO_2

Hydrothitsiol dimethyl ether forms only a mononitro-derivative (XI). Urushiol is accordingly but one member of a considerable group of related substances, derivatives of catechol substituted in both 3- and 4-positions by saturated and unsaturated normal chains identical with those which occur in the higher fatty acids. The novelty and interest of this work need not be emphasised.

Hyssop plants attacked by fungi contain a rhamno-glucoside, hyssopin, $C_{50}H_{66}O_{30},3H_2O$, which yields hyssopinglycone, $C_{16}H_{14}O_6$, on hydrolysis.[93] The latter appears to be an analogue of butein (XII), which is produced by the action of alkali on butin, a constituent of *Butea frondosa*.[94] Hyssopinglycone, an ochre-yellow, crystalline substance, is hydrolysed by hot 33 per cent. aqueous potassium hydroxide with formation of phloroglucinol and aceto-piperone (XIII).

It should therefore have the formula XIV, especially since butein, when similarly treated, gives resacetophenone, but the constitution actually advanced is XV, in which the aromatic groups are transposed.

(XII.) HO OH OH CH_3·CO O CH_2 (XIII.)
CO·CH:CH OH O

HO OH O CH_2 HO OH O CH_2
CH:CH·CO O CO·CH:CH O
OH OH
(XIV.)   (XV.)

[93] O. A. Oesterle, *Schweiz. Apoth. Ztg.*, 1921, **59**, 548; *A.*, i, 849; *ibid.*, 1922, **60**, 441; *Chem. Zentr.*, 1922, iii, 1300. It has only been possible to consult the abstracts.

[94] A. G. Perkin and J. J. Hummel, *T.*, 1904, **85**, 1459.

Chrysophanic acid has been synthesised and thus definitely proved to be 1 : 8-dihydroxy-3-methylanthraquinone (XVI).[95]

(XVI.)

The details of the method employed follow normal lines, the starting points being α-nitrophthalic anhydride and m-cresol. At the same time the constitutions of rhein and aloemodin are finally decided, since these two substances and chrysophanic acid are known to differ only in the side chain, which is —CO_2H, —$CH_2 \cdot OH$, and —CH_3, respectively.

Polycyclic Groups.

As usual, a great amount of systematic work in the naphthalene and anthracene series has been published during the past year, and the new availability of tetrahydronaphthalene has naturally been exploited to the full. In view, however, of the existence of Reports on the Progress of Technological Chemistry, the discussion of these subjects may be confined to the remark, in no way deprecatory, that the literature has been enriched by the description of vast numbers of new compounds.

In view of the importance of boric acid in the chemistry of anthracene derivatives, the isolation of definite boric compounds in the anthraquinone group is of interest.[96] 1-Hydroxyanthraquinone is transformed by the action of a solution of boric acid in acetic anhydride into 1-hydroxyanthraquinonyl boroacetate, $C_{14}H_7O_2 \cdot O \cdot B(OAc)_2$, which loses a molecule of acetic anhydride on heating in a vacuum, yielding the metaborate, $C_{14}H_7O_2 \cdot O \cdot BO$, but 2-hydroxyanthraquinone does not behave in a parallel manner. This is but one instance of a characteristic difference in behaviour of hydroxyl groups in the α- and β-positions in the anthraquinone nucleus and it is clearly a question of some kind of association, in the former case, of the hydroxyl with the neighbouring carbonyl. The stability of the boroacetate already mentioned can, for example, be roughly represented by formula I. This is confirmed by the facts that 1 : 5-dihydroxyanthraquinone reacts with two molecules of boroacetic anhydride, the 1 : 8-isomeride with one only, and 1 : 4 : 5-trihydroxyanthraquinone suffers boroacetylation of two hydroxyls and acetylation of the third. The difficulty experienced in acetylating 1-hydroxyanthraquinones is also ascribed to a mutual partial valency saturation of the hydroxyl and carbonyl groups and this theory serves to explain why chrysazin is more readily mono-

[95] R. Eder and C. Widmer, *Helv. Chim. Acta*, 1922, **5**, 3; *A.*, i, 260.

[96] O. Dimroth and T. Faust, *Ber.*, 1921, **54**, [*B*], 3020; *A.*, i, 155.

acetylated than anthrarufin. The carbonyl group is supposed to be unable to neutralise more than one of the hydroxyls in the α-position. Relations between the quinone oxygen and auxochromes in the α-position have also been postulated in order to account for the tinctorial and dyeing properties of members of the anthraquinone group and it is worthy of note that the more useful dyestuffs belong to the 1 : 4- or 1 : 5-series, in which both carbonyls can so function. In addition, the plan of increasing the number of auxochromes in anthraquinone dyestuff-types seldom produces the desirable results which may have been anticipated. In the chlorate–alkali fusion of benzanthrone, which converts this substance into 2-hydroxybenzanthrone (II) it has been found that the yield becomes almost quantitative when anthraquinone is added to the mixture.[97] The constitution of the substance, which may also be obtained by the action of glycerol and sulphuric acid on 2-hydroxyanthranol, has been proved by the identification of the product of oxidation of its methyl ether with 2-methoxyanthraquinone-1-carboxylic acid (III).[98]

(I.)   (II.)   (III.)

Reduction of anthraquinone to anthranol is readily effected by heating with dextrose and alkali solution under pressure,[99] but when the reaction was applied to 2-hydroxyanthraquinone the main product was the acid IV. This readily forms a lactone and its methyl ether yields III and other substances on oxidation. It is possible to replace the dextrose used by other carbohydrates, and even by glycerol, which must clearly undergo condensation before it can supply the necessary chain of four carbon atoms.[1]

(IV.)

[97] A. G. Perkin and G. D. Spencer, *T.*, 1922, **121**, 474.
[98] A. G. Perkin, *ibid.*, 1920, **117**, 698.
[99] *Idem.*, Brit. Pat. 151707, 1920.
[1] G. G. Bradshaw and A. G. Perkin, *T.*, 1922, **121**, 911.

A direct synthesis of pyrene from naphthalene has been carried out and the stages are as indicated in the following scheme. The starting point is obtained by the condensation of naphthalene and malonyl bromide in presence of aluminium chloride, and the substance VI by an analogous method applied to V.[2]

$$CH_2Ph\cdot C(OEt)_3 \longrightarrow CHPh\text{:}C(OEt)_2 + C_2H_4 + H_2O.$$

Miscellaneous.

Benzaldehyde-copper.—Nickel, iron, and aluminium have no action on benzaldehyde, but lead and magnesium dissolve to a yellowish-brown solution, zinc to a greenish-brown, silver to a brownish-black, cobalt to a brown, and copper to a green solution. In the case of copper, the substance formed is a green additive product, $(Ph\cdot CHO)_2Cu$, which can be crystallised from toluene. It is remarkably stable, being unattacked by dilute hydrochloric acid or alkalis, but is oxidised to benzoic acid by dilute nitric acid. The constitution of the compound is not yet clear, the obvious possibility that it is copper hydrobenzoin being difficult to reconcile with the stability to acid.[3]

Enolisation of Acids.—The acetal of phenylketen can be prepared by careful distillation of the ortho-ester of phenylacetic acid with phosphoric acid in a vacuum : [4]

$$CH_2Ph\cdot C(OEt)_3 \longrightarrow CHPh\text{:}C(OEt)_2 + C_2H_4 + H_2O.$$

Compared with keten, it is quite stable, but is attacked by water with formation of ethyl phenylacetate and by bromine with formation of ethyl phenylbromoacetate. The metallic derivatives of

[2] K. Fleischer and E. Retze, *Ber.*, 1922, **55**, [*B*], 3280; *A.*, i, 1138.

[3] A. L. Bernoulli and F. Schaaf, *Helv. Chim. Acta*, 1922, **5**, 721; *A.*, i, 1029.

[4] H. Staudinger and G. Rathsam, *ibid.*, 645; *A.*, i, 1014.

carboxylic esters such as malonic ester are in all probability analog-ously constituted and contain the group :C(OEt)·OM. This hypo-thesis is supported by the behaviour of the potassio-derivatives of diphenylacetic acid and its ester, since these are highly unsaturated substances.[5] Potassamide reacts with ethyl diphenylacetate in liquid ammonia to form an additive product which, on heating in a vacuum at 100—120°, loses ammonia, yielding potassoxyethoxy-diphenylketen, CPh_2:C(OEt)·OK. This salt is spontaneously oxidised by oxygen and on treatment with methyl iodide gives ethyl αα-diphenylpropionate, $CPh_2Me·CO_2Et$. It reacts with diphenyl-keten to form tetraphenylacetone and tetraphenylallene and although the production of the latter is said to be difficult to explain, it appears to fall into line with the usual schemes of addition and division :

$$\begin{array}{ccc} Ph_2C{:}C(OEt)\cdot OK & Ph_2C{-}C(OEt)\cdot OK & Ph_2C \\ Ph_2C{:}C{:}O & \longrightarrow \quad Ph_2C{:}C{-}O \quad \longrightarrow & Ph_2C{:}C \end{array} + KEtCO_3.$$

The reaction affords further proof, if that were necessary, of the constitution assigned to the potassium derivative. When potassium diphenylacetate is treated with potassamide in liquid ammonia solution, it yields an amorphous, yellow precipitate of the composi-tion and formula, CPh_2:C(OK)$_2$. This substance is at once oxidised by oxygen with production of an explosive peroxide, but careful treatment in toluene solution with air gives a monoxide probably

having the structure, $\overset{Ph_2C}{\underset{O}{\Large>}}C(OK)_2$, because aqueous acids or

alkalis change it into benzilic acid. Alkylation of the dipotassoxy-compound with methyl iodide produces potassium αα-diphenyl-propionate, whilst the action of methyl sulphate results in the formation of the corresponding methyl ester. These experiments provide further evidence that the metallic derivatives of the enolised forms of esters are directly alkylated on the carbon. Possibly the most satisfactory representation of sodio-compounds of the familiar type is as complex compounds, for example, [CN·CH·CO$_2$Et]Na, in which formula the bonds merely represent the mode of linking of atoms and have no implications in regard to the distribution of affinity. The problem of relative ease of enolisation of acids and their derivatives can also be attacked by stereochemical methods, and the racemisation of optically acid amides has been studied from this point of view.[6] Of the substances examined, d-tartamide, d-α-hydroxy-β-phenylpropionamide, $CH_2Ph·CH(OH)·CO·NH_2$, l-β-hydroxy-β-phenylpropionamide, $HO·CHPh·CH_2·CO·NH_2$, d-mono-

[5] H. Staudinger and P. Meyer, *Helv. Chim. Acta*, 1922, **5**, 656; *A.*, i, 1015.

[6] A. McKenzie and (Miss) I. A. Smith, *T.*, 1922, **121**, 1348.

ethoxysuccinamide, and l-atrolactinamide, $HO \cdot CPhMe \cdot CO \cdot NH_2$, were not racemised in cold alcoholic solution in presence of small quantities of potassium hydroxide. On the other hand, d-dimethoxysuccinamide, l-monomethoxysuccinamide, and l-mandeloethylamide were slowly racemised in similar circumstances, and l-mandelamide, l-phenylmethoxyacetamide, and l-phenyl-p-tolylacetamide exhibited the phenomenon with increasing facility in the order named.

The latter observation is explained by the increased mobility of the hydrogen atom in the α-position which is the result of the high valency demands of the alkyloxy and aryl groups as illustrated in the expression :

$$\begin{array}{c} Ph \\ C_7H_7 \end{array} {>} C {\stackrel{\displaystyle H}{\diagdown}} CO \cdot NH_2 .$$

There has been much activity during the year in connexion with aryl derivatives of boron, phosphorus, arsenic, chromium, bismuth, lead, thallium, and other elements, but it has not been found possible to include a section dealing with the results, which are nevertheless of very considerable interest.

R. ROBINSON.

PART III.—HETEROCYCLIC DIVISION.

THERE are no outstanding features to which particular attention may be directed in this Report. Rather the year has been one of quiet progress and consolidation of previous work, involving in several directions a revision of earlier conclusions.

Ring Formation and Stability.

Some years ago, it was suggested [1] that the points of attachment to a carbon atom of two groups, known to exert steric hindrance, are normally, in virtue of their large molecular volume, further apart than would be indicated by the regular tetrahedral distribution. The view has since been developed [2] that, in general, each atom attached to a carbon atom occupies a spherical domain,

[1] J. Kenner, $T.$, 1914, **105**, 2688.

[2] C. K. Ingold, $ibid.$, 1921, **119**, 305.

the cubic content of which is proportional to its atomic volume. By calculation on this basis, the following values were deduced for the angle, 2δ, subtended by two carbon atoms attached to a central carbon atom, carrying two other groups, RR′ :

RR′.	H,H.	H,Me.	Me,Me.	Et,Et.	$(CH_2)_2$.	$(CH_2)_3$.
2δ	115·3°	112·5°	109·5°	107°	116·9°	113·0°
k'	11·2	2·28	0·551	0·146	13·8	2·63

The last two values are for a pair of carbon atoms attached to a *cyclo*propane and to a *cyclo*butane ring, respectively, and are derived on the assumption that the position of these is such as to trisect the solid angle round the central carbon atom and external to the ring.[3] This would seem to be a logical extension of Werner's view as to the cause of the regular tetrahedral distribution of four similar groups attached to a carbon atom, and the experimental evidence in favour of the corollary appears to be a valuable confirmation of the main proposition.

In the above table, k' is proportional to the velocity constants of hydrolysis of the hydantoins by baryta :

$$R_2C{<}{}^{NH\cdot CO}_{CO-NH} \rightarrow R_2C{<}{}^{NH\cdot CO\cdot NH_2}_{CO\cdot OH} \ .$$

The agreement between the order of the constants and that of the values of 2δ is regarded as confirming the accuracy of the method of calculating 2δ.[4] It will be noted, however, that the values quoted for 2δ are not properly applicable to this case, in which one carbon atom is replaced by a nitrogen atom, more especially as the atomic volume of the latter is very small.[5] The order of the corrected values for 2δ will, however, very possibly be the same and thus correspond with those of k', although it is less certain that this will also hold for the *cyclo*-propylene and -butylene residues. It may also be suggested that other atoms than those immediately attached to the central carbon atom must be included in such considerations, and it is perhaps in recognition of this that the values quoted for the methyl and ethyl groups differ.

It has long been known that when the quaternary ammonium bromides (I) and (II) are heated with ammonia, they are converted into the compounds (III) and (IV) : [6]

[3] R. M. Beesley, C. K. Ingold, and J. F. Thorpe, *T.*, 1915, **107**, 1080.

[4] C. K. Ingold, S. Sako, and J. F. Thorpe, *ibid.*, 1922, **121**, 1177.

[5] I. Traube, *Annalen*, 1895, **290**, 119; *A.*, 1896, ii, 354.

[6] M. Scholtz, *Ber.*, 1891, **24**, 2402; 1898, **31**, 1700; *A.*, 1891, i, 1353; 1898, i, 567.

$$
\underset{\text{(I.)}}{\left[\begin{array}{c}\text{CH}_2\\\text{CH}_2\end{array}\right]\!\!>\!\!\underset{\text{Br}}{\text{N}}\!\!<\!\!\left[\begin{array}{c}\text{CH}_2\\\text{CH}_2\end{array}\right]} \rightarrow \underset{\text{(III.)}}{\left[\begin{array}{c}\text{CH}_2\!\cdot\!\text{NH}\!\cdot\!\text{CH}_2\\\text{CH}_2\!\cdot\!\text{NH}\!\cdot\!\text{CH}_2\end{array}\right]} \rightarrow
$$

$$
\underset{\text{(V.)}}{2\left[\begin{array}{c}\text{CH}_2\\\text{CH}_2\end{array}\right]\!\!>\!\!\text{NH}} \qquad \underset{\text{(II.)}}{\left[\begin{array}{c}\text{CH}_2\\\text{CH}_2\end{array}\right]\!\!>\!\!\underset{\text{Br}}{\text{N}}[\text{CH}_2]_5} \rightarrow
$$

$$
\underset{\text{(IV.)}}{\left[\begin{array}{c}\text{CH}_2\!\cdot\!\text{NH}\!\cdot\!\text{CH}_2\!\cdot\!\text{CH}_2\\\text{CH}_2\!\cdot\!\text{NH}\!\cdot\!\text{CH}_2\!\cdot\!\text{CH}_2\end{array}\right]\!\!>\!\!\text{CH}_2} \rightarrow
$$

$$
\left[\begin{array}{c}\text{CH}_2\\\text{CH}_2\end{array}\right]\!\!>\!\!\text{NH} + \text{NH}\!\!<\!\!\left[\begin{array}{c}\text{CH}_2\!\cdot\!\text{CH}_2\\\text{CH}_2\!\cdot\!\text{CH}_2\end{array}\right]\!\!>\!\!\text{CH}_2
$$

It may be that this change is simply due to the tendency of quaternary ammonium compounds to pass under such conditions into derivatives of tervalent nitrogen. In any case, the instability of the resulting bisimines is indicated by the fact that at 250° they break down into dihydro*iso*indole (V) accompanied in the second case by piperidine. Dihydro*iso*indole is in fact most conveniently prepared by heating (I) with ammonia solution at 250°.[7]

Hexamethyleneimine (I) is obtained in 50 per cent. yield by heating hexamethylenediamine hydrochloride,[8] although octa-[9] and deca-methylenediamines [10] furnish butyl- and hexyl-pyrrolidines, respectively. The result recalls the direct formation of 2-methylhexamethyleneimine by the reduction of methyl ε-amino-amyl ketone (II) : [11]

$$
\text{(I.)}\quad \begin{array}{c}\text{CH}_2\!\cdot\!\text{CH}_2\!\cdot\!\text{CH}_2\\\text{CH}_2\!\cdot\!\text{CH}_2\!\cdot\!\text{CH}_2\end{array}\!\!>\!\!\text{NH} \qquad \text{(II.)}\quad [\text{CH}_2]_5\!\!<\!\!\begin{array}{c}\text{COMe}\\\text{NH}_2\end{array} \rightarrow [\text{CH}_2]_5\!\!<\!\!\begin{array}{c}\text{CHMe}\\\text{NH}\end{array}
$$

It will perhaps be well to consider these results, and, for example, the good yield of suberone obtainable from calcium suberate,[12] in the light of recent suggestions [13] that polymethylene rings containing more than five carbon atoms are free from tension and have not a plane configuration.

The results of earlier work [14] on the relative stability of cyclic

[7] J. v. Braun and (Miss) A. Nelken, *Ber.*, 1922, **55**, [*B*], 2059; *A.*, i, 863.

[8] F. Schmidt, *ibid.*, 1584; *A.*, i, 761.

[9] J. v. Braun and C. Müller, *ibid.*, 1906, **39**, 4110; *A.*, 1907, i, 28.

[10] F. Krafft, *ibid.*, 2193; *A.*, 1906, i, 553.

[11] S. Gabriel, *ibid.*, 1909, **42**, 1259; *A.*, 1909, i, 492.

[12] J. N. E. Day, G. A. R. Kon, and A. Stevenson, *T.*, 1920, **119**, 639.

[13] W. Huckel, *Ber.*, 1920, **53**, 1277; *A.*, 1920, i, 603; H. G. Derx, *Rec. trav. chim.*, 1922, **41**, 312; *A.*, i, 651.

[14] Compare *Ann. Reports*, 1920, p. 103.

structures containing nitrogen have been supplemented and summarised.[15] Neither a 2-, 3-, 4-methyl-, nor a 5 : 6-methylenedioxy-group affects the behaviour of N-methyltetrahydroquinoline methochloride towards sodium amalgam, although that of dihydroindole is considerably modified by either a 2- or a 3-methyl group.[16] As might be anticipated, a 2- or 3-phenyl group has a marked effect on the tetrahydroquinoline structure.[17] The difference between the results obtained by different methods of degrading such structures is illustrated by the case of methyl*iso*chondodendrine. By exhaustive methylation two methines are obtained, whereas the sodium amalgam method yields one product only.[18]

Attention was directed in last year's Report [19] to a compound, in which tendencies towards two distinct modes of intramolecular condensation seemed to be evenly balanced. Another instance of this kind is now provided by the conversion of 6-methoxyindole-2-carboxydimethylacetalylmethylamide (I) under the influence of alcoholic hydrochloric acid into a mixture of methoxyketomethyldihydrocarboline (II) and methoxyketomethyldihydroindolediazine (III) :

It is not easy to explain the fact that the presence of the methyl group attached to the nitrogen atom in the side chain should determine carboline formation, as contrasted with the conversion of indole-2-carboxyacetalylamide itself into ketodihydroindolediazine. If no nuclear methoxyl group be present, the course of the reaction will be entirely towards carboline formation, but it is seen from the diagram that the effect of the methoxyl group is to diminish the " positive " character of the methenyl hydrogen atom of the indole nucleus, concerned in the reaction, and to enhance that of the imino-hydrogen atom necessary for indolediazine

[15] J. v. Braun and J. Seeman, *Ber.*, 1922, **55**, [*B*], 3818; *A.*, 1923, i, 146.

[16] J. v. Braun, K. Heide, and L. Neumann, *ibid.*, 1916, **49**, 2613; *A.*, 1916, i, 742.

[17] J. v. Braun, J. Seeman, and A. Schultheiss, *ibid.*, 1922, **55**, [*B*], 3803; *A.*, 1923, i, 138.

[18] F. Faltis and F. Neumann, *Monatsh.*, 1921, **42**, 311; *A.*, i, 569.

[19] p. 112.

formation.[20] If this explanation be correct, it may be expected that a 5- or 7-methoxyl group will favour carboline formation. Such an influence of the position of methyl groups on the formation and stability of coumaranones has been noticed in previous Reports.[21] In this connexion, too, the results of an amplification [22] of earlier work on the velocities of hydrolysis of 2-substituted benzoxazoles are of interest.

A different effect of substituents, which is superimposed on that associated with their orientation, and results in a modification of the general condition of the molecule, is illustrated by the fact that neither of the three nitrophenoxyacetyl chlorides is convertible into a coumaranone,[23] although the reaction is otherwise a fairly general one.[24]

The synthesis of methyl*iso*propylcoumaranone (I) by its aid [25] is another illustration of the relative independence of intramolecular condensation on steric influences.[26] This point stands out more clearly when it is noted that the rupture of the ring usually brought about by intermolecular hydrolysis of coumaranones, and of their *iso*nitroso-derivatives, does not occur in this case, possibly owing to steric protection.

It is suggested [27] that the formation of cyclic additive products, for example (II), by interaction of aldehydes, ketones, or αβ-unsaturated ketones and phosphorus trichloride, or compounds derived from it by replacement of one or two chlorine atoms by phenyl-, phenoxy-, or ethoxy-groups,

resembles the conversion of ammonia into ammonium compounds in that in that in each case the tervalent atom develops two latent valencies

[20] W. O. Kermack, W. H. Perkin, and R. Robinson, *T.*, 1922, **121**, 1872.

[21] *Ann. Reports*, 1920, **16**, 101; 1921, **18**, 108.

[22] S. Skraup and (Miss) S. Moser, *Ber.*, 1922, **55**, [*B*], 1080; *A.*, i, 574; compare *Ann. Report*, 1920, **16**, 99.

[23] T. H. Minton and H. Stephen, *T.*, 1922, **121**, 1591.

[24] *Ibid.* 1598.

[25] E. Mameli, *Gazzetta*, 1922, **52**, [i], 322; *A.*, i, 669.

[26] Compare *Ann. Reports*, 1921, **18**, 108.

[27] J. B. Conant, *J. Amer. Chem. Soc.*, 1921, **43**, 1705; *A.*, i, 41; J. B. Conant, A. D. MacDonald, and A. Mc. B. Kinney, *ibid.*, 1923; *A.*, i, 186; compare *Ann. Reports*, 1920, **17**, 98.

, of opposite signs.[28]   The course of this process in its initial stages in, for example, the addition of phosphorus trichloride to a carbonyl group is conceived to be as follows.   The positive nucleus of the carbon atom is assumed to be exposed, through the drawing away of its two electrons, shared with the oxygen octet, and to attract unshared electrons of the phosphorus atom.   In the resulting system, the oxygen and phosphorus atoms are respectively negatively and positively charged, and therefore an inner polar bond is set up between them.

The reactions of the hydrazodicarbon-mono- and -di-thiocarbon-amides provide illustrations of the principle that every chemical system tends towards that condition in which the maximum of chemical neutralisation is attained.[29]   For example, when hydrazo-monomethyldicarbonthiamide (I) is boiled in acid solution, the basic iminothiodiazole methyl ether (II) and ammonia are formed, whilst in caustic alkaline solution, the acidic iminothiourazole (III) and methyl mercaptan produced :

$$\underset{\text{(III.)}}{\overset{\text{NH·NH}}{\underset{\text{NH}}{\text{HN:C}\quad\text{C}}}} + \text{MeSH} \overset{\text{NaOH}}{\longleftarrow} \underset{\text{(I.)}}{\overset{\text{NH·NH}}{\underset{\text{NH NH}}{\text{HS·C}\quad\text{C·SMe}}}} \overset{\text{HCl}}{\longrightarrow} \underset{\text{(II.)}}{\overset{\text{NH·N}}{\underset{\text{S}}{\text{HN:C}\quad\text{C·SMe}}}} + \text{NH}_3$$

The constitution of the compounds of type (II) is confirmed by their synthesis by condensation of thiosemicarbazides with carbon disulphide in presence of alcoholic potassium hydroxide.   An interesting case is that of the hydrazide (IV), from which in acid solution iminothiodiazolone (V), and in alkaline solution the sodium salt of thiourazole (VI) are formed as chief product :

$$\underset{\text{(IV.)}}{\overset{\text{NH-NH}}{\underset{\text{PhNH NH}_2}{\text{CO CS}}}} \longrightarrow \underset{\text{(VII.)}}{\left[\overset{\text{N—NH}}{\underset{\text{NH}_2}{\text{CO CS}}}\right]} \quad \underset{\text{(V.)}}{\overset{\text{NH·NH}}{\underset{\text{S}}{\text{CO C:NH}}}} \quad \underset{\text{(VI.)}}{\overset{\text{NH·NH}}{\underset{\text{NH}}{\text{CO CS}}}}$$

The same intermediate product (VII) may be assumed in each case.[30]

[28] Compare also (Mrs.) G. M. Robinson and R. Robinson, *T.*, 1917, **111**, 958; *Ann. Reports*, 1917, **16**, 134.

[29] A. Michael, *J. pr. Chem.*, 1899, [ii], **60**, 292; *A.*, 1900, i, 321.

[30] F. Arndt and E. Milde, *Ber.*, 1921, **54**, [*B*], 2089; F. Arndt, E. Milde, and F. Tschenscher, *ibid.*, 1922, **55**, [*B*], 341; *A.*, 1921, i, 842; 1922, i, 375; compare E. Fromm, *ibid.*, 1921, **54**, [*B*], 2840; *Annalen*, 1922, **426**, 313; *A.*, i, 62, 377; P. C. Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502, 1510; *A.*, i, 875, 876.

The formation of cyaphenines by distillation of aryliminoalkyl ethers

$$3Ar\cdot C{<}^{NH}_{OR} \rightarrow ArC{<}^{N\cdot CAr}_{N:CAr}{>} + 3R\cdot OH$$

is attributed to special reactivity of nascent nitriles, since these suffer polymerisation only at high temperatures or under the influence of catalysts.[31] The change, however, occurs, although with extreme slowness, at the ordinary temperature and therefore might possibly consist in polymerisation, followed by elimination of alcohol.

Reference has previously been made to the difficulty frequently attaching to the production of systems containing rings in straight alignment on either side of a benzene ring.[32] This is noticeable in the poor yield of 2 : 3-naphthindigotin from 3-carboxy-2-naphthyl-glycine : [33]

In passing, it may be noted that 8-carboxy-1-naphthylglycine could not be converted into a *peri*-naphthindigotin.[34] Again, when 6-aminotetrahydroquinoline was submitted to the quinaldine synthesis, a phenanthroline resulted.[35] On the other hand, 2 : 6-dihydroxy-*m*-αα-benzbispyrrole is readily produced by reduction of 4 : 6-dinitrophenylene-1 : 3-diacetic acid with ferrous sulphate and ammonia :[36]

Two instances of the indirect formation of structures of the general form just referred to may also be noticed here, although the primary reaction does not involve a benzene nucleus. In each case the starting material is 2 : 3-dichloro-α-naphthaquinone. This, by successive treatment with aniline and with sodium sulphide, is converted into 2-anilino-3-mercapto-1: 4-naphthaquinone (I), from

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[31] T. B. Johnson and L. W. Bass, *J. Amer. Chem. Soc.*, 1922, **44**, 1341; *A.*, i, 736.

[32] *Ann. Reports*, 1921, **18**, 109.

[33] H. E. Fierz and R. Tobler, *Helv. Chim. Acta*, 1922, **5**, 557; *A.*, i, 869.

[34] H. E. Fierz and R. Sallmann, *ibid.*, 560; *A.*, i, 870.

[35] J. Lindner, *Monatsh.*, 1921, **42**, 421; *A.*, i, 687.

[36] W. Davies and E. H. C. Hickox, *T.*, 1922, **121**, 2640.

which ββ-naphthaphenthiazine-6 : 11-quinone (II) is obtained by atmospheric oxidation in alcoholic solution.

(I.)   (II.)   (III.)

The parent naphthaphenthiazine (III) is prepared from this by energetic reduction with stannous chloride.[37]   Again, the original quinone, when treated with sodium sulphide in absence of air, yields the green monosodium salt of the internal quinhydrone (I), from which 5 : 7 : 12 : 14-tetrahydroxydibenzothianthrene (II) is obtained by acid or alkaline reduction :

(I.)   (II.)   (III.)

A noteworthy reaction is the elimination of sulphur with formation of dinaphthathiophendiquinone (III), when the diquinone derived from (I) is heated above its melting point in boiling nitrobenzene solution or with concentrated sulphuric acid.[38]

Isomerism.

Further noteworthy cases of isomerism in the indazole series have been recorded.   Freshly prepared 5-chloroindazole melts at 119—120°, but changes, slowly at the ordinary temperature, and fairly rapidly at 100°, into a modification, m. p. 143—144°. Similarly, the 5-bromo-derivative exists in a labile form, m. p. 124—125°, and a stable form, m. p. 132—133°.   Since each form may be recovered unchanged after recrystallisation, they would seem not to be polymorphous.   The failure to convert the high-melting into the low-melting isomerides suggests that their relationship is not one of structural isomerism, whilst the higher melting point of the stable isomerides is in agreement with the hypothesis of stereoisomerism, represented by (IV) and (V),

[37] K. Fries and F. Kerkow, *Annalen,* 1922, **427**, 281; *A.,* i, 577.
[38] K. Brass and L. Kohler, *Ber.,* 1922, **55**, [*B*], 2543; *A.,* i, 1050.

and already applied to the 2-acylindazoles.[39]   In agreement with this analogy, 3-halogen indazoles do not exhibit isomerism.

A fuller investigation [40] of the two forms of 3-phenylindazole, m. p. 107—108° and 115—116° [41] has shown these to be inter-convertible, and, further, it would seem that the low-melting isomeride is the more stable, since it may be obtained from the other form by distillation.   The relationship is therefore considered to be one of structural isomerism :

The same explanation is adopted in the case of two forms of 3 : 5-diphenyl*iso*oxazole-4-carboxylic acid (I) and (II), and of the corre sponding 5-phenyl-3-methyl-derivative.

$$\text{(I.)} \quad O{<}^{\text{CPh:C·CO}_2\text{H}}_{\text{N==CPh}} \qquad\qquad O{<}^{\text{CPh·C·CO}_2\text{H}}_{\text{N—CPh}} \quad \text{(II.)}$$

In each case, the acid of lower melting point is converted by boiling caustic alkali into its isomeride, although the reverse change has not been accomplished.   It is hoped that further information may be gained from attempts to resolve the acids into optically active components, since the compound represented by (II) should be capable of resolution.[42]   It will be noted that the structural formulæ assigned to these pairs of compounds correspond closely with those of the tautomeric forms of dimethyl*dicyclo*pentanone-carboxylic acid.[43]   It is interesting to note how in three distinct fields of investigation, the suggestion is almost simultaneously forthcoming that the types of bridged and unsaturated ring systems here considered are closely related.   At the same time, it must be observed that although the indazoles are benzopyrazoles, the tendency on the part of pyrazoles to assume the bridged structure, if existent, is very limited.[44]

[39] K. v. Auwers and H. Lange, *Ber.*, 1922, **55**, [B], 1139; *A.*, i, 684.
[40] K. v. Auwers and A. Sondheimer, *ibid.*, 1896, **29**, 1255; *A.*, 1896, i, 503.
[41] K. v. Auwers and K. Hüttener, *ibid.*, 1922, **55**, [B], 1112; *A.*, i, 682.
[42] M. Betti and others, *Gazzetta*, 1915, **45**, i, 362; ii, 151, 377; 1921, **51**, ii, 229; *A.*, 1915, i, 997; 1916, i, 222; 1922, i, 52.
[43] E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *T.*, 1922, **121**, 128.
[44] K. v. Auwers and H. Broche, *Ber.*, 1922, **55**, [B], 3880; *A.*, 1923, i, 151.

The rearrangement of 2-hydroxy-3-phenylindazole (A), when boiled with caustic alkali, has now been shown to consist in the interchange of the hydroxyl and the phenyl groups,[45] since the product furnishes azobenzene-o-carboxylic acid on oxidation and is identical with 3-hydroxy-2-phenylindazole (I), prepared from hydrazobenzene-o-carboxylic acid : [46]

It is considered that the isomerisation depends rather on a direct interchange of the groups concerned than on the formation of any transient additive product.

Isomeric forms of five-membered cyclic compounds have also been observed in the pyrazolone series. Two isomerides result from the methylation of 3-phenyl-5-pyrazolone (II). Of these, one, m. p. 96°, is probably a methoxy-derivative, but the other, m. p. 165°, is converted by phosphorus pentachloride into 5-chloro-3-phenyl-1-methylpyrazole [47] (IV), identical with the product previously obtained from 3-phenyl-1-methyl-5-pyrazolone, m. p. 207° [48] (V) :

A similar statement in regard to the 1-phenyl-5-methyl derivative is already on record.[49] The suggestion is made that these pairs of compounds may be stereoisomerides represented by (VI) and of the type already mentioned in the case of the indazoles. It will, however, be noticed that no interconversion has been accomplished in the present instance and that in the case of indazoles the experimental evidence is to the effect that substitution in the position corresponding with that occupied by the hydroxyl group in (VI) inhibits stereoisomerism.

[45] K. v. Auwers and A. Sondheimer, *loc. cit.*

[46] P. Freundler, *Compt. rend.*, 1906, **143**, 909; *Bull. Soc. chim.*, 1911, [iv], **9**, 738; *A.*, 1907, i, 158; 1911, i, 753.

[47] C. A. Rojahn, *Ber.*, 1922, **55**, [*B*], 2959, 3990; *A.*, i, 1183.

[48] R. v. Rothenburg, *J. pr. Chem.*, 1895, [ii], **52**, 23; *A.*, 1895, i, 686; A. Michaelis, *Annalen*, 1907, **352**, 152; *A.*, 1907, i, 246.

[49] F. Stolz, *J. pr. Chem.*, 1897, [ii], **55**, 164; *A.*, 1897, i, 374.

It would appear, in fact, that, apart from the careful attempts at discrimination noted in the cases of the indazoles, the suggestions made in some of the other cases just mentioned are *ad hoc* in character, and to be received with corresponding reserve.

Further, instances have not been lacking during the year which show the need for caution, before cases of alleged isomerism are finally accepted. Thus, the "*iso*isatogens," obtained from isatogens by the action of alcoholic hydrogen chloride,[50] are now stated to be in reality additive compounds of isatogens with alcohol, and to be formed, although more slowly, by treatment with alcohol alone. In the case of ethyl isatogenate, the reaction is expressed as follows :

$$C_6H_4\!<\!^{CO}_{NO}\!>\!C\cdot CO_2Et \rightarrow C_6H_4\!<\!^{CO}_{N-}\!>\!C\!<\!^{CO_2Et}_{OR}\! \rightarrow C_6H_4\!<\!^{CO_2H}_{NH\cdot CO\cdot CO_2H}$$
$$\overset{|}{O}H \qquad\qquad (I.)$$

The additive compounds are hydrolysed by cold caustic alkali to N-oxalylanthranilic acid (I).[51]

Again, the suggestion that the isatoids represent isomeric forms of isatin [52] has turned out to be wrong.[53] These compounds, more correctly termed isatoid monoalkyl ethers, were originally prepared [54] by interaction of alkyl iodides and the silver salt of isatin, and also from the alkylisatins, which are the first product of the reaction, by spontaneous evaporation of their benzene solutions while exposed to light. By hydrolysis, they are converted into anhydro-indoxyl-α-anthranilide (II), the constitution of which is indicated by its oxidation to the known anhydro-α-isatinanthranilide (III) :

(II.)   (III.)

The last compound is also obtained directly from the original ethers when their alkaline solutions are exposed to light. The existence of isomerides of isatin [55] is still in dispute, and it is maintained that certain of these are in reality isatoid derivatives.

[50] *Ann. Reports*, 1919, **15**, 109; 1921, **17**, 116.

[51] G. Heller and W. Bolsaneck, *Ber.*, 1922, **55**, [B], 474; *A.*, i, 369.

[52] A. Hantzsch, *ibid.*, 1921, **54**, [B], 1221; *A.*, 1921, i, 597.

[53] G. Heller and W. Benade, *ibid.*, 1922, **55**, [B], 1006; *A.*, i, 582; A. Hantzsch, *ibid.*, 3180; *A.*, i, 1177.

[54] A. v. Baeyer and Oeconomides, *ibid.*, 1882, **15**, 2093; *A.*, 1883, 201.

[55] A. Hantzsch, *ibid.*; G. Heller, *ibid.*, 2681; *A.*, i, 1058; compare *Ann. Reports*, 1921, **17**, 116.

Stereoisomerism.

Although there has been no novel development in the stereo-chemistry of heterocyclic compounds during the period under review, a number of interesting applications have been made of known principles. Besides those already referred to, they are mentioned in connexion with catechin (p. 146), picrorocellin (p. 151), bishydrocarbostyril-3 : 3'-spiran (p. 152), quinine (p. 157), anhydro-ecgonine (p. 160), and scopolamine (p. 161).

Alkylation.

The sodium salt of 5-chloro-3-methylpyrazole gives rise to 3-chloro-1 : 5-dialkyl derivatives.[56] This result is the more inter-esting since 1 : 5-dialkylpyrazoles themselves seem incapable of existence. Thus, alkylation of 3-alkylpyrazoles furnishes a 1 : 3-, but no 1 : 5-derivative. All attempts to synthesise the latter have failed, and even when 1 : 5-dimethylpyrazoline is oxidised, 1 : 3-dimethylpyrazole is formed. Similarly, although 1-phenyl-3-methylpyrazole methiodide is converted into 1-phenyl-3-methyl-pyrazole by heat, the corresponding 1-benzyl-compound yields 1 : 3-dimethylpyrazole under these conditions : [57]

$$\begin{array}{ccc} \text{CH} & \text{CHMe} & \\ \| & \| & \\ \text{CH} - \text{N} \diagdown^{\text{Me}}_{\text{I}} & \longrightarrow & \\ & & \\ \dot{\text{N}}\text{B}_2 & & \dot{\text{N}}\text{Mc} \end{array} \qquad \begin{array}{c} \text{CH} - \text{CMe} \\ \| \quad \| \\ \text{CH} \quad \text{N} \end{array}$$

The properties of the methylation product from the sodium salt of 5-chloro-3-phenylpyrazole differ from those attributed to either of the products which might have been expected.[58] The alkyl-ation of 3-phenyl-5-pyrazolone has already been referred to.

Alkylation of 3-phenylindazole leads to results varying with the conditions employed, but there is a predominant tendency for the substituent to enter the 1-position.[59]

A new dimethyl derivative has been prepared by treating leuco-indigotin in persistently alkaline solution with methyl sulphate. This is considered to be an *O*-substituted compound, since it is converted by nitrous acid into indigotin, and by chromic acid into isatin.[60]

There are grounds for the belief that alkylation of the glyoxalines does not proceed by direct replacement of an imino-hydrogen

[56] C. A. Rojahn, *Ber.*, 1922, **55**, [*B*], 2959; *A.*, i, 1183.

[57] K. v. Auwers and H. Broche, *ibid.*, 3880; *A.*, 1923, i, 151.

[58] C. A. Rojahn, *loc. cit.*

[59] K. v. Auwers and K. Hüttener, *Ber.*, 1922, **55**, [*B*], 112; *A.*, i, 682.

[60] E. Grandmougin, *Compt. rend.*, 1922, **174**, 758; *A.*, i, 470.

atom, and the following scheme is put forward for the case of 4-nitro-5-methylglyoxaline : [61]

$$O_2N \cdot C \!\!-\!\! N \!\!\diagdown\!\!\!\underset{MeC \cdot NH}{\overset{\|}{\diagup}} CH \rightarrow \left[O_2N \cdot C \!\!-\!\! N \!\!-\!\! Me \!\!\diagdown\!\!\!\underset{MeC \cdot NH}{\overset{\overset{SO_4Me}{|}}{\diagup}} CH \right] \rightarrow O_2N \cdot C \cdot NMe \!\!\diagdown\!\!\!\underset{MeC \!\!-\!\! N}{\overset{\|}{\diagup}} CH$$

A 1 : 3-dimethyl derivative is obtained by the action of diazomethane on uracil.[62]

Five-membered Heterocyclic Structures.

The formula of the elsholtzic acid derived from the action of amyl nitrite and sodium ethoxide on elsholtzione [63] has now been confirmed by its oxidation to furan-2 : 3-dicarboxylic acid. The constitution of this in turn is decided by its preparation from the chloride of synthetic [64] 2-methylfuran-3-carboxylic acid. Bromination of this compound occurs partly in the side chain and partly in the nucleus, so that hydrolysis of the product furnishes a bromo-2-hydroxymethylfuran-3-carboxylic acid. This undergoes oxidation to the corresponding dicarboxylic acid, from which the bromine is removed by means of zinc dust and ammonium chloride.[65]

The possibility of synthesising coumarins by condensation of phenol or their ethers with fumaric, maleic, or malic acid has been investigated, but with somewhat discordant results.[66]

A closer examination of the product of the action of acetylene on finely divided iron pyrites at 300° has shown that whilst thiophen constitutes 40 per cent. of the whole, it is accompanied by its 2- and 3-methyl and -ethyl derivatives, as well as by a number of other products, which do not contain sulphur.[67]

The resemblance between thiophen and benzene extends to their behaviour towards ethyl diazoacetate. In the former case, reaction only occurs at 130° in presence of an excess of thiophen. The product, obtained in poor yield, is probably ethyl dicyclo-Δ^2-α-penthiophen-5-carboxylate, $\underset{CH \cdot S \cdot CH}{\overset{CH \!\!-\!\! CH}{|}} \!\!\diagdown\!\! CH \cdot CO_2Et$,[68] since it

[61] F. L. Pyman, *T.*, 1922, **121**, 2619.

[62] T. B. Johnson, A. J. Hill, and F. H. Case, *Proc. Nat. Acad. Sci.*, 1922, **8**, 44; *A.*, i, 471.

[63] Compare *Ann. Reports*, 1920, **16**, 114.

[64] E. Benary, *Ber.*, 1911, **44**, 493; *A.*, 1911, i, 319.

[65] Y. Asahina and S. Kuwada, *J. Pharm. Soc. Japan*, 1922, **485**, 565; *A.*, i, 1047.

[66] G. C. Bailey and F. Boettner, *J. Ind. Eng. Chem.*, 1921, **18**, 905; *A.*, 1921, i, 879; W. Ponndorf, D.R.-P. 338737; *A.*, i, 565.

[67] W. Steinkopf and J. Herold, *Annalen*, 1922, **428**, 123; *A.*, i, 850; compare W. Steinkopf, *Annalen*, 1914, **403**, 11; *A.*, 1914, i, 425.

[68] W. S. Steinkopf and H. Augestad-Jensen, *ibid.*, 154; *A.*, i, 851.

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easily forms an amide, and therefore probably contains a secondary rather than a tertiary carbon atom in the α-position to the carbethoxy-group.[69]

The catalytic reduction of pyrrole in presence of nickel at 200° results in the opening of the ring in every possible manner, since ammonia, diethylamine, methyl-*n*-propylamine, and *n*-butylamine are formed. The production of *n*-amylamine and ethyl-*n*-propylamine at the same time is attributed to the preliminary formation of piperidine through the intermediary of *N*-methylpyrrole.[70]

It has been shown [71] that the pyrrole nucleus is amenable to the Gattermann synthesis of aldehydes by means of hydrogen cyanide, and that, as the formulæ (I) and (II) show, substitution may occur in the α- as well as in the β-position.

$$\begin{array}{cc}
\text{MeC---C·CO}_2\text{Et} & \text{HCO·C---C·CO}_2\text{Et} \\
\text{(I.)} \quad \text{HCO·C} \quad \text{CMe} & \text{MeC} \quad \text{CMe} \quad \text{(II.)} \\
\text{NH} & \text{NH}
\end{array}$$

In view of this result, and the known similarity in reactivity between pyrrole and phenol, it is not surprising that the Hoesch synthesis also may be applied to pyrrole. The use of cyanogen or malononitrile in this connexion results in the formation of cyanoketones, and not of diketones.[72]

Not only acetyl or carboxyl,[73] but also methyl groups [74] are replaceable in the pyrrole nucleus by the nitro-group through the agency of nitric acid. The following formulæ, in which the groups which suffer replacement are indicated by heavy type, suggest that the order of replaceability is acetyl, methyl, and carbethoxyl :

$$\begin{array}{cc}
\text{MeC---C·CO}_2\text{Et} & \text{MeC---C·\textbf{COMe}} \\
(\textbf{HCO} \text{ or) } \textbf{COMe}\text{·C} \quad \text{CMe} & \text{EtO}_2\text{C·C} \quad \text{CMe} \\
\text{NH} & \text{NH}
\end{array}$$

$$\begin{array}{c}
\textbf{MeC}\text{---C·CO}_2\text{Et} \\
\text{EtO}_2\text{C·C} \quad \text{C\textbf{Me}} \\
\text{NH}
\end{array}$$

The formula (III) is suggested for tripyrrole, from a determination

[69] Compare E. Fischer and W. Dilthey, *Ber.*, 1902, **35**, 844; *A.*, 1902, i, 269.

[70] N. J. Putochin, *ibid.*, 1922, **55**, [B], 2742; *A.*, i, 1176.

[71] H. Fischer and W. Zerweck, *ibid.*, 1942; *A.*, i, 758.

[72] H. Fischer, K. Schnelle, and W. Zerweck, *ibid.*, 2390; *A.*, i, 1055.

[73] G. Ciamician and H. Silber, *ibid.*, 1885, **18**, 1456; 1886, **19**, 1078; *A.*, 1885, 992; 1886, i, 718.

[74] H. Fischer and W. Zerweck, *ibid.*, 1922, **55**, [B], 1949; *A.*, i, 758.

of the α-positions available for coupling with diazomium compounds and the formation of succinic acid by oxidation with chromic acid. For similar reasons, hydroxydipyrrole is considered to be (IV) or the corresponding ketone.[75]

$$\text{(III.)} \quad \begin{array}{c} \text{CH}-\text{CH} \\ \text{CH} \quad \text{C} \end{array}\!\!\diagdown\!\!\diagup\!\! \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ -\text{CH} \end{array} \quad \begin{array}{c} \text{CH}-\text{CH} \\ \text{CH}-\text{C} \end{array}\!\!\diagdown\!\!\diagup\!\! \begin{array}{c} \\ \text{CH} \end{array}$$
$$\text{NH} \qquad \text{NH} \qquad \text{NH}$$

$$\begin{array}{c} \text{CH}-\text{CH} \\ \text{CH} \quad \text{C} \end{array}\!\!\diagdown\!\!\diagup\!\! \begin{array}{c} \text{CH}-\text{CH} \\ -\text{C} \end{array}\!\!\diagdown\!\!\diagup\!\! \begin{array}{c} \\ \text{C}\cdot\text{OH} \end{array} \text{(IV.)}$$
$$\text{NH} \qquad \text{NH}$$

By distillation of chitin with zinc dust, a mixture of bases is obtained, which contains some pyridine derivatives, but consists chiefly of pyrroles. Of the latter, one appears to be identical with synthetic α-methyl-N-n-hexylpyrrole, and in consequence it is suggested that the grouping (I) is present in chitin.[76]

$$\begin{array}{c} -\text{CH}-\!\!-\!\!-\text{CH(OH)}\cdot\text{CH}_2\cdot\text{OH} \\ \text{CH(OH)}-\text{CH}-\!\!-\!\!-\text{NH}\cdot\text{CH}\cdot\text{NH}\cdot\text{CH(OH)}\cdot\text{CH}\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{OH} \\ -\text{O}-\!\!- \end{array}$$

(I.)

In a review [77] of the various explanations which have been offered of the Fischer indole synthesis, preference is given to that which [78] postulates the intermediate formation of an anil :

$$\text{NHPh}\cdot\text{N:CR}\cdot\text{CH}_2\text{R} + \text{H}_2 \longrightarrow \text{NH}_2\text{Ph} + \text{NH:CR}\cdot\text{CH}_2\text{R}$$
$$\uparrow \qquad\qquad\qquad \downarrow$$
$$\text{C}_6\text{H}_4\!\!<\!\!\begin{array}{c}\text{CHR}\\ -\text{N}\end{array}\!\!>\!\!\text{CR} + \text{H}_2 \longleftarrow \text{NPh:CR}\cdot\text{CH}_2\text{R} + \text{NH}_3$$

In order to explain the extension of the reaction to phenylmethyl-hydrazones, it is assumed that the ketimine formed in the first stage of the reaction may react in the aminic form, $\text{NH}_2\cdot\text{CR:CHR}$. Reference may be made here to the synthesis of the indenoindoles (II) and (III) by heating the phenylmethylhydrazones of α- and β-hydrindones, respectively, with concentrated hydrochloric acid.[79]

The pyrogenetic synthesis of indole by passing a mixture of

[75] A. Pieroni and A. Moggi, *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 381; *A.*, i, 766.

[76] P. Karrer and A. P. Smirnoff, *Helv. Chim. Acta*, 1922, **5**, 832; *A.*, 1923, i, 122.

[77] C. Hollins, *J. Amer. Chem. Soc.*, 1922, **44**, 1598; *A.*, i, 863.

[78] G. Reddelien, *Annalen*, 1912, **388**, 179; *A.*, 1912, i, 363.

[79] J. W. Armit and R. Robinson, *T.*, 1922, **121**, 827.

aniline vapour, acetylene, and carbon dioxide through an iron tube at 700° is moderately successful. A quantity of crude indole was collected amounting, in the most favourable case,[80] to 34 per cent. by weight of the aniline not recovered.

A new synthesis of r-tryptophan has been described. Indole is successively converted into magnesium β-indolyl bromide, and β-aldehydoindole, which is then condensed with hydantoin by the Perkin reaction to β-indolalhydantoin. Reduction with sodium-amalgam, followed by hydrolysis, completes the synthesis : [81]

The catalytic reduction of N-methyl- or -ethyl-carbazole in presence of nickel salts at 215° under pressure and in absence of a solvent furnishes, besides unchanged material, a mixture of the tetrahydro-derivative, insoluble in acid, and the basic octahydro-derivative (I), from which a decahydro-derivative (II) is obtained by the action of tin and hydrochloric acid. The constitution of the deoxy-base (III), derived from this, follows from its hydrolysis by acids to 2-Δ¹-$cyclo$hexenyl$cyclo$hexanone (IV) : [82]

The result is of interest as indicating that the formation of pyrrolines (corresponding with II) from pyrroles proceeds simply by the

[80] R. Majima, T. Unno, and K. Ono, *Ber.*, 1922, **55**, [*B*], 3854; *A.*, 1923, i, 135.

[81] R. Majima and M. Kotake, *ibid.*, 385§; *A.*, 1923, i, 156.

[82] J. v. Braun and H. Ritter, *ibid.*, 3792; *A.*, 1923, i, 141.

reduction of one double bond rather than by reduction of the conjugated system, followed by isomerisation.

The formation of indigotin by alkaline fusion of dianilidofumaric acid, from aniline and dibromofumaric acid, has been described.[83]

6 : 6'-Dibromoindigotin has been isolated from the fluid expressed from certain varieties of cockle, which the natives of Mexico have long utilised for dyeing purposes.[84]

Formulæ reminiscent of the indigoid type have been assigned to the product (I) of the oxidation of rhodanine by ferric chloride,[85] and, provisionally, to "naphthothiam blue," (II) the leuco-compound of which is formed when 1 : 8-nitronaphthalenesulphinic acid is reduced with zinc dust and potassium sulphite.[86]

In accordance with the relationship, previously noticed, between the constitution of benzoxazole derivatives and their capacity for visible fluorescence,[87] (III) exhibits this property, but (IV) and (V) do not.[88]

Imino-oxazolidines (VI) result from the condensation of styrene dibromides with carbamide :

Their hydrolysis with alkali hydroxides provides a new method for the preparation of alkamines.[89]

[83] G. C. Bailey and R. S. Potter, *J. Amer. Chem. Soc.*, 1922, **44**, 215; *A.*, i, 370.

[84] P. Friedlaender, *Ber.*, 1922, **55**, [*B*], 1655; *A.*, i, 793.

[85] C. Gränacher, H. Reis, and E. Pool, *Helv. Chim. Acta*, 1922, **5**, 382; *A.*, i, 576.

[86] A. Reissert, *Ber.*, 1922, **55**, [*B*], 858; *A.*, i, 583.

[87] Compare *Ann. Reports*, 1921, **18**, 127.

[88] F. Henrich, H. Suntheimer, and C. Steinmann, *Ber.*, 1922, **55**, [*B*], 3911; *A.*, 1923, i, 145.

[89] J. Takeda and S. Kuroda, *J. Pharm. Soc. Japan*, 1919, **449**, 561; 1921, 1; *A.*, 1920, i, 228; 1922, i, 272.

The evidence of the non-existence of 1 : 5-dialkylpyrazoles has already been summarised (p. 136). This forms a basis for an adverse criticism of Knorr's view that one hydrogen atom in the pyrazole nucleus is oscillatory and it is suggested that the cause of the apparent identity of 3- and 5-derivatives of pyrazole, on which this view is based, is again the instability of one form, and its consequent transition to the other.[90]

A study of the electrochemical oxidation of pyrazoles has shown that, in acid suspension, the heterocyclic nucleus of 1-phenyl-3-methylpyrazole is destroyed, but that in presence of potassium carbonate solution, the benzene nucleus is destroyed, with formation of pyrazole-3-carboxylic acid.[91]

The applicability of the Friedel-Crafts reaction to 5-chloropyrazoles, giving rise to substitution in the 4-position, is limited to 1-aryl derivatives and to the chlorides of aromatic acids.[92]

The difficulty associated with the original explanation of the behaviour of the 5-nitroglyoxalines on reduction was indicated in a previous Report.[93] dl-Alanine-N-methylamidine (I) has since been found among the reduction products of 5-nitro-1 : 4-dimethylglyoxaline (prepared by nitration of 1 : 4-dimethylglyoxaline). Accordingly, the reaction is now considered to be analogous to the rupture of the glyoxaline ring by means of benzoyl chloride and sodium hydroxide, and in the case referred to is represented as follows :

$$\begin{array}{c} NO_2 \cdot C \cdot NMe \\ MeC \!-\! N \end{array}\!\!\!>\!\!CH \rightarrow \begin{array}{c} NH_2 \cdot C \vdots NMe \\ \text{(I.) } MeCH \cdot NH_2 \end{array} \rightarrow \begin{array}{c} CO_2H \\ MeCH \cdot NH_2 \end{array} + CH_3 \cdot NH_2 + NH_3$$

4-Nitro-1 : 5-dimethylglyoxaline, from the nitration of 1 : 5-dimethylglyoxaline, yielded the amino-compound, with dl-N-methylalanine and ammonia.[94] These results confirm the orientations provisionally adopted [95] for the above two dimethyl derivatives, when they were prepared from 4-methylglyoxaline, and also the suggestion that pilocarpine is a 1 : 5-derivative of glyoxaline. Considerations of space prevent more than a reference to the discussion of the behaviour of the glyoxalines on alkylation (compare p. 136) and towards benzoyl chloride and sodium hydroxide from the point of view of polarity. The inadequacy of earlier suggestions in regard to the latter reaction is indicated in a review

[90] K. v. Auwers and H. Broche, *Ber.*, 1922, **55**, [B], 3880; *A.*, 1923, i, 151.
[91] Fr. Fichter and H. de Montmollin, *Helv. Chim. Acta*, 1922, **5**, 256; *A.*, i, 470.
[92] C. A. Rojahn, *Ber.*, 1922, **55**, [B], 291; *A.*, i, 373.
[93] *Ann. Reports*, 1920, **17**, 115.
[94] F. L. Pyman, *T.*, 1922, **121**, 2616.
[95] *Idem, ibid.*, 1910, **97**, 1814.

of this,[96] in which it is shown that the ring may also be opened by means of *iso*valeryl chloride. Neither benzenesulphonyl chloride nor acetic anhydride, however, is effective. The result in the last case is the more striking, since the same reagent opens the benzoglyoxaline ring,[97] and yet the latter is the more resistant towards benzoyl chloride and pyridine. These reactions permit the conversion of glyoxalines into 2-alkyl derivatives, since it has been shown [98] that when, for example, bisbenzoylaminopropylene (I), derived from 5-methylglyoxaline, is heated with the anhydride of an aliphatic acid, 2-alkyl-5-methylglyoxaline is produced :

$$\begin{array}{c} \text{MeC·NH} \\ \text{CH·N} \end{array}\!\!\!>\!\!\text{CH} \rightarrow \quad \text{(I.)} \quad \begin{array}{c} \text{MeC·NHBz} \\ \text{CH·NHBz} \end{array} \rightarrow \quad \begin{array}{c} \text{MeC·NH} \\ \text{CH·N} \end{array}\!\!\!>\!\!\text{CR}$$

The polybromo-compounds resulting from the direct halogenation of glyoxalines may be converted into monobromo-derivatives by treatment with sodium sulphite solution.[99]

The rearrangement of the system (I) in certain compounds to furnish 1 : 2 : 3 : 4-tetrazoles would appear to be an intramolecular reaction comparable with the familiar intermolecular saturation of a double bond by the action of diazo-compounds :

$$\text{(I.)} \quad \begin{array}{c} -\text{C:N}- \\ \text{N}_3 \end{array} \rightarrow \begin{array}{c} -\text{C}-\text{N}- \\ \text{N} \quad \text{N} \\ \diagdown\diagup \\ \text{N} \end{array} \quad \begin{array}{l} \text{CPh·Cl:N·N:CHPh} \quad \text{(II.)} \\ \text{NPh:C:NPh} \quad \text{(III.)} \end{array}$$

Suitable azides of the type (I) are generated as intermediate products (not isolated) by interaction of sodium azide and benzylidene-benzhydrazide chloride (II) or carbodiphenyldi-imide (III), or, in place of the latter, a mixture of a thiourea or a thiosemicarbazide with lead oxide.[1] Again, when mustard oils are heated with azoimide in an indifferent solvent, cyanamides are formed as intermediate products :

$$\text{R·N·CS} + \text{HN}_3 \rightarrow \text{R·NH·CS·N}_3 \rightarrow \text{R·NH·C:N} \quad \begin{array}{c} \text{HS·C}-\text{NPh} \\ \text{N} \quad \text{N} \\ \diagdown\diagup \\ \text{N} \end{array} \quad \text{(V.)}$$
$$\text{(IV.)}$$

[96] A. Windaus, W. Dörries, and H. Jenssen, *Ber.*, 1921, **54**, [*B*], 2745; *A.*, i, 60.

[97] G. Heller, *ibid.*, 1904, **37**, 3115; *A.*, 1904, i, 942.

[98] A. Windaus and W. Langenbeck, *ibid.*, 1922, **55**, [*B*], 3706; *A.*, 1923, i, 147.

[99] I. E. Balaban and F. L. Pyman, *T.*, 1922, **121**, 947; L. Light and F. L. Pyman, *ibid.*, 2626.

[1] R. Stollé, *Ber.*, 1922, **55**, [*B*], 1289; R. Stollé and A. Netz, *ibid.*, 1297; *A.*, i, 689, 690.

These then react with more azimide to form tetrazoles. 5-Mercapto-1-phenyl-1 : 2 : 3 : 4-tetrazole (V) is formed when phenylcarbimide is boiled with an alcoholic suspension of sodium azide, or when the corresponding thiocarbamic azide (type IV) is treated with alkali.[2]

ψ-Aniline (VI) is the sole product of the interaction of sulphuryl azide, $SO_2(N_3)_2$, and benzene at 140°,[3] but from p-xylene, a mixture of ψ-p-xylidine with a base, possibly (VII), and a solid of the same composition, are formed.[4] The products obtained when benzyl azide is heated with p-xylene, on the other hand, are entirely derived from the azide, and include (VIII) and (IX) : [5]

(VI.)   (VII.)   (VIII.)   (IX.)

The interaction of thiobenzilic acid and benzaldehyde in presence of hydrogen chloride leads to the formation of triphenyl-1 : 3-oxthiophan-5-one (I). This, on treatment with cold concentrated sulphuric acid, yields a product, to which the formula (II) is assigned on the grounds of its conversion into 9-phenylanthracene by distillation with zinc dust, and of its insolubility in alkali.[6]

(I.)   (II.)

The Pyrone Group.

The method whereby pyrylium salts are synthesised by condensation of an o-hydroxybenzaldehyde with a compound containing the $\cdot CH_2 \cdot CO \cdot$ group [7] has been shown [8] to be applicable

[2] E. Oliveri-Mandalà, *Gazzetta*, 1921, **51**, ii, 195; 1922, **52**, i, 101; *A.*, 1921, i, 900; 1922, i, 473.

[3] F. Schmidt, *Ber.*, 1922, **55**, [B], 1581; *A.*, i, 777.

[4] T. Curtius and F. Schmidt, *ibid.*, 1571; *A.*, i, 776.

[5] T. Curtius and G. Ehrhardt, *ibid.*, 1559; *A.*, i, 775.

[6] A. Bistrzycki and B. Brenken, *Helv. Chim. Acta*, 1922, **5**, 20; *A.*, i, 268.

[7] W. H. Perkin and R. Robinson, *P.*, 1907, **19**, 149; H. Decker and T. v. Fellenberg, *Ber.*, 1907, **40**, 3815; *Annalen*, 1907, **356**, 281; *A.*, 1907, i, 950.

[8] D. D. Pratt and R. Robinson, *T.*, 1922, **121**, 1577.

to ω-ethoxy- and -phenoxy-acetophenones, yielding compounds (I) of the anthocyanidin type.

(I.)   (II.)

(III.)

The blue anthocyanidin pigments have been considered to be alkali salts of phenol betaines, for example (II). This view has, however, been criticised [9] on the ground that it cannot be applied to the colour change of solutions of 4'-hydroxy-2-styrylbenzopyrylium chloride from red to blue on dilution with water, in absence of any base. The change is attributed to production of the quinonoid compound (or, less probably, a corresponding betaine) (III). The pyrylium compound in question is synthesised by the action of hydrogen chloride on a solution of o-hydroxystyryl methyl ketone and p-hydroxybenzaldehyde in formic acid.

A synthesis of isohæmatein tetramethyl ether ferrichloride (IV) has been carried out [10] by reactions precisely analogous to those used in the case of isobrazilein trimethyl ether.[11]

(IV.)

Demethylation of the above ferrichloride by means of hydrochloric acid furnished a product identical with the isohæmatein from hæmatoxylin.[12]

No definite conclusion has yet been reached in the controversy [13]

[9] J. S. Buck and I. M. Heilbron, T., 1922, **121**, 1198.

[10] H. G. Crabtree and R. Robinson, ibid., 1033.

[11] Compare Ann. Reports, 1918, **15**, 104.

[12] J. J. Hummel and A. G. Perkin, T., 1882, **41**, 373.

[13] Ann. Reports, 1920, **17**, 110; 1921, **18**, 129; A. C. von Euler, Svensk. Kem. Tidskr., 1921, **33**, 88; A., i, 45.

regarding the constitution of catechin. The crystallographic evidence in favour of a formula of the $\alpha\gamma$-diphenylpropane type has been met with equally definite evidence of the same character in favour of the $\alpha\alpha$-type of formula.[14] An intimation [15] that the discrepancies are to be subjected to independent investigation is therefore to be welcomed. In this paper, the optical activity of acacatechin is denied. On the other hand, the optical activity of the pentacetyl derivatives of three samples of catechin has been independently affirmed,[16] and evidence of a somewhat ingenious type is also offered of the presence of two asymmetric carbon atoms in the catechin molecule. In the course of the latter investigation, dl-epicatechin was prepared, and then detected in Pegu-catechu.[17]

The Pyrimidines.

Two new syntheses of pyrimidine derivatives have been recorded. Mono- and di-alkylmalonic esters condense with aromatic amidines in presence of sodium ethoxide, yielding respectively insoluble yellow (I), and soluble colourless derivatives (II) : [18]

$$\text{(I.)} \quad RC\underset{C(OH):N}{\overset{C(OH)\cdot N}{<}}\!\!\!>CAr \qquad R_2C\underset{CO\cdot NH}{\overset{CO-N}{<}}\!\!\!>CAr \quad \text{(II.)}$$

The condensation products of aldehydes with asparagine furnish good yields of hydroxybromopyrimidinecarboxylic acids on oxidation with alkaline solutions of sodium hypobromite :

$$\begin{array}{ccc} H_2N-CO & & NH\cdot CO \\ RCHCH_2 & \rightarrow & RC \quad CBr \\ N-CH\cdot CO_2Na & & N-C\cdot CO_2Na \end{array}$$

The unbrominated compounds may be obtained by use of potassium permanganate, but the yields are not so good. The presence of asparagine in young etiolated shoots has prompted the suggestion that a reaction similar to these may produce the pyrimidines and purine bases found in nucleoproteins.[19]

The desulphurisation of 9-alkyl-8-thiouric acids by treatment with nitrous acid leads to the formation of xanthines (III) :

$$\begin{array}{cccc} -C\cdot NH & & -C-N & -C-NR & -C\cdot NHR \\ \overset{|}{-}\overset{|}{C\cdot NR}>CS \rightarrow & -C\cdot NR>CH & -C\cdot NR'\!\!\gg C \rightarrow & -C\cdot NHR \\ \text{(III.)} & \text{(IV.)} & & \text{(V.)} \end{array}$$

[14] M. Nierenstein, *T.*, 1922, **121**, 604.

[15] M. Nierenstein, *Ber.*, 1922, **55**, [B], 3831.

[16] K. Feist and A. Futtemenger, *ibid.*, 942; *A.*, i, 565.

[17] K. Freudenberg, O. Böhme, and L. Purrmann, *ibid.*, 1734; *A.*, i, 756; K. Freudenberg, *ibid.*, 1938; *A.*, i, 756.

[18] A. W. Dox and L. Yoder, *J. Amer. Chem. Soc.*, 1922, **44**, 311; *A.*, i, 374.

[19] E. Cherbuliez and K. N. Stavritch, *Helv. Chim. Acta*, 1922, **5**, 267; *A.*, i, 581.

When the reaction is extended to 7 : 9-dialkyl-8-thiouric acids, sulphur is again removed, but the alkyl groups and the pyrimidine ring remain intact. In accordance with the formula (IV) assigned to the resulting deoxyuric acids, acid hydrolysis gives rise to dialkyluracils (V), the monoformyl derivatives of which are obtained by alkaline hydrolysis.[20]

Betaines.

The discordance between the ordinary formulæ for the various types of betaines, including certain dyestuffs like gallocyanine, rosindone, and cyanidine, and the usual stereochemical conceptions is well known. It has now been suggested [21] that the betaine structure is not cyclic in the ordinary sense, but represents a dipolar unit, for example (I),

$$\overset{-}{O}\cdot OC\cdot R\cdot \overset{+}{N}Me_3 \qquad IMe_3N\cdot C_6H_4\cdot \underset{CH\cdot CO_2Me}{\overset{|}{C}H} \qquad \longrightarrow \qquad \overset{+}{Me_3}N\cdot C_6H_4\cdot \underset{CH\cdot CO\cdot \overset{-}{O}}{\overset{|}{C}H}$$

(I.)   (II.)

containing within itself the opposite charges carried by the sodium and chlorine ions in solid sodium chloride. The analogy supplies an explanation of the high melting point and the low solubility in organic solvents which characterise the amino-acids and betaines.[22] In further confirmation of this view, it has been shown that a betaine results from the hydrolysis of the quaternary methiodide of methyl *trans-p*-dimethylaminocinnamate (II).[23] Similarly, the salts of dibasic acids with multivalent metals are to be compared with calcium carbonate.

Carnitine is now considered to be a β-betaine (III), since it shows the behaviour of a β-hydroxy-acid, in that it suffers dehydration to *apo*carnitine by concentrated sulphuric acid at 130°.[24] This reaction distinguishes carnitine from the synthetic product,[25] with which it had previously been thought identical. The formula also explains the formation of β-bromobetaine (IV) from carnitine on oxidation.[26]

$$(III.) \quad \overset{+}{Me_3}N\cdot CH_2\cdot \underset{\overset{|}{CO\cdot \overset{-}{O}}}{C}H\cdot CH_2\cdot OH \qquad \overset{+}{Me_3}N\cdot CH_2\cdot \underset{\overset{|}{CO\cdot \overset{-}{O}}}{C}H_2 \quad (IV.)$$

Apophyllenic acid is probably a 4- (I) rather than a 3-betaine,

[20] H. Biltz and others, *Annalen*, 1922, **426**, 237—299; *A*., i, 380—384.

[21] P. Pfeiffer, *Ber.*, 1922, **55**, [B], 1762; *A*., i, 720.

[22] Compare A. Reis, *Z. Physik*, 1920, **1**, 204; *A*., 1920, ii, 537.

[23] P. Pfeiffer and G. Haefelin, *Ber.*, 1922, **55**, [B], 1769; *A*., i, 738.

[24] R. Engeland, *ibid.*, 1921, **54**, [B], 2208; *A*., 1921, i, 880.

[25] E. Fischer and A. Göddertz, *ibid.*, 1911, **44**, 3279; *A*., 1911, i, 19.

[26] R. Engeland, *ibid.*, 1909, **42**, 2457; *A*., 1909, i, 551.

since synthetic 3-methyl 4-ethyl 2 : 6-dimethylcinchomeronate [27] is converted by treatment with methyl iodide and moist silver oxide into methyl, not ethyl, 2 : 6-dimethylapophyllenate (II) :

(I.) CO·O / CO_2H / + NMe   → CO_2Et / Me, CO_2Me, Me / N   →   (II.) CO·O / Me, CO_2Me, Me / + NMe

The new betaine notation furnishes a possible explanation of the apparent anomaly that silver apophyllenate is not converted by methyl iodide into methyl apophyllenate, but into the isomeric betaine.[28]

The ·Pyridine Group.

Attention may be directed to a discussion of the separation of pyridine, and its methyl and dimethyl derivatives from coal tar oil in a state of purity.[29]

A formula of the type (I) is suggested [30] in place of the usual ketonic formula for the γ-pyridones, on the ground that these do not show ketonic reactions and are colourless. Although an additive compound (II) of

(II.) OMe / N / Ph, I   ⇄   O / NPh / (I.)   →   (III.) OMgMe / N / Ph, I

of N-phenylpyridone with methyl iodide may be prepared,[31] its properties are not those of a true ammonium iodide, since the corresponding hydroxide reverts to the pyridone when its solution is evaporated, as does the additive compound of the pyridone with magnesium methyl iodide (III) when treated with acid. Further, the changes observable during the course of the reaction between chelidonic acid and amines suggest that this occurs in three stages, which are thus represented :

[27] Compare *Ann. Reports*, 1918, **15**, 101.

[28] O. Mumm and E. Gottschaldt, *Ber.*, 1922, **55**, [B], 2064, 2075; *A.*, i, 861, 862.

[29] J. G. Heap, W. J. Jones, and J. B. Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936; *A.*, i, 171.

[30] A. P. Smirnoff, *Helv. Chim. Acta*, 1921, **4**, 599; *A.*, 1921, i, 594; *Ber.*, 1922, **55**, [B], 612; *A.*, i, 464.

[31] W. Borsche and I. Bonacker, *Ber.*, 1921, **54**, [B], 2678; *A.*, i, 50.

(IV.)

In the first, at the ordinary temperature the pyrone ring is opened. In the second, a homogeneous coloured fluid melt is produced, which in the third stage passes into the colourless final product. Corresponding with (IV), a yellow p-tolyl derivative was isolated, and shown to furnish a phenylhydrazone.

A comparison of the ketone (V), synthesised in the usual manner,[32] with the corresponding ethyl ketones, N-methyl-conhydrinone and -*iso*pelletierin, has shown that it resembles the latter rather than the former in its ready semicarbazone formation, but that its carbonyl group is not so easily reduced to a methylene group as

(V.)   (VI.)

that of either of the others. All attempts, whether by direct or by indirect demethylation, to prepare piperidylethanone (VI) were unsuccessful.

The condensation of α-picoline methiodide with p-dimethylamino-benzaldehyde results in the formation of a product (I), which constitutes the most powerful sensitiser yet known for green light for gelatino-silver bromide photographic plates.[33]

(I.) Me_2N〈—〉—CH:CH—〈 〉   NMeI

Interpretations of the reactions ensuing on the partial reduction of the pyridine nucleus[34] have been considerably revised, as a result of parallel investigations. Of these, perhaps the most illuminating are those concerned with the formation and reactions

[32] K. Hess and W. Corleis, *Ber.*, 1921, **54**, [B], 3010; *A.*, i, 170.

[33] W. H. Mills and (Sir) W. J. Pope, *T.*, 1922, **121**, 946.

[34] Compare *Ann. Reports*, 1920, **17**, 106; 1921, **18**, 134.

of diacetyltetrahydrodipyridyl.[35] This colourless compound, when prepared from pyridine, is accompanied by a small proportion of an orange product, identified as diacetyldihydrodipyridyl (II). This is easily oxidised by air or by bromine to $\gamma\gamma$-dipyridyl, or its perbromide, respectively, and may be obtained by adding acetic anhydride to the blue solution produced when dipyridyl is reduced by zinc dust and acetic acid.[36] It seems not to be directly obtainable from the tetrahydro-derivative, but is produced when this is heated with dipyridyl in acetic anhydride solution at 100° :

The significance of this lies in the fact that hot solutions of the tetrahydro-compound become blue only in presence of air (which is known to produce dipyridyl), or on the addition of dipyridyl. The blue colour therefore appears to be associated with the presence in solution of dihydrodipyridyl or a derivative. This inference is confirmed by the composition of " dipyridyl violet chloride " (I), prepared by reduction of dipyridyl with one equivalent of chromous chloride in presence of calcium chloride :

It will be noted that this compound differs from most quinhydrones in that the quinonoid portion is the reduced part of the molecule, and becomes aromatic by oxidation.

It has been recognised that the blue solutions obtained from the brown "benzoylpyridinium," yellow dimethyl- and diethyl- "tetrahydrodipyridyls," and red " benzylpyridinium," most probably owe their origin to similar reactions. The last compound has been definitely recognised as NN-dibenzyldihydro-$\gamma\gamma$-dipyridyl, but an account of this work is unnecessary, since in many respects the results are analogous to those just detailed. The obvious inference from the above that hydrogen atoms in the γ-position of the pyridine nuclei of the parent compounds are essential to

[35] O. Dimroth and F. Frister, *Ber.*, 1922, **55**, [B], 1223, 3693; *A.*, i, 678.

[36] The earlier statement, that the tetrahydro-compound is formed by this reaction, has been withdrawn; *loc. cit.*, 1223, footnote 2.

the production of blue solutions has been confirmed by an examination of the corresponding $\gamma\gamma$-dicollidyl and di-2 : 4-lutidyl compounds.[37]

Picrorocellin.

Picrorocellin is the colourless mono-O-ether of 2′ : 5-diketo-3 : 6-di-ω-hydroxybenzyl-1-methylpiperazine (I),[38] since on treatment with hydrochloric and acetic acids, it is converted into pale yellow xanthorocellin (II). The constitution of this product follows from its oxidation to benzaldehyde (and benzoic acid), and 2 : 3 : 5 : 6-tetraketo-1-methylhexahydro-1 : 4-diazine (III), identical with the compound [39] prepared by condensation of methyloxamide and oxalyl chloride. Since, further, methylation of the secondary amino- and the free hydroxyl groups of picrorocellin yields an internally compensated product, it follows that this, and hence probably also picrorocellin itself, has a *trans*-configuration.

OH·CHPh·CH·NMe·CO   → CHPh:C·NMe—CO   → CO·NMe·C(
  CO·NH—CH·CHPh·OH   CO·NH·C:CHPh   CO·NH—C(
      (I.)   (II.)   (III.)

The Quinoline Group.

Quinoline and its derivatives rapidly absorb four atomic proportions of hydrogen in their pyridine nuclei, when they are reduced in presence of nickel salts under pressure, but the subsequent stages of reduction to decahydro-derivatives proceed much more slowly.[40]

The synthesis of cinchonic and quinic acids has continued to engage attention. The preparation of cinchonic acid by decomposition of the quinoline-2 : 4-dicarboxylic acid [41] resulting from the condensation of pyruvic acid with isatin has been extended to 6-methoxyisatin for the purpose of preparing quinic acid.[42] But the process would not seem to be as convenient as that in which 6-methoxyquinoline serves as a starting material.[43] Another process is outlined in the following scheme :

[37] B. Emmert and others, *Ber.*, 1921, **54**, [B], 3168; 1922, **55**, [B], 1352, 2322; E. Weitz and others, *ibid.*, 395, 599, 2864; *A.*, i, 179, 680, 1064, 365, 470, 1186.

[38] M. O. Forster and W. B. Saville, *T.*, 1922, **121**, 816.

[39] J. V. Dubsky, *Ber.*, 1919, **52**, 216; *A.*, 1919, i, 288.

[40] J. v. Braun, A. Petzold, and J. Seeman, *ibid.*, 1922, **55**, [B], 3779; *A.*, 1923, i, 136.

[41] W. Pfitzinger, *J. pr. Chem.*, 1902, [ii], **66**, 263; *A.*, 1903, i, 53.

[42] J. Halberkann, *Ber.*, 1921, **54**, [B], 3079; *A.*, i, 172.

[43] A. Kaufmann, *ibid.*, 1922, **55**, [B], 614; *A.*, i, 464.

$$\underset{\text{NMe·COMe}}{\bigodot} + (CO_2Et)_2 \xrightarrow{\text{Na}} \underset{\text{NMe·CO}}{\bigodot} CO\!<\!\overset{CO_2Et}{\underset{CH_2}{}} \xrightarrow{H_2SO_4}$$

$$\underset{\underset{NMe}{\overset{}{\bigodot}}}{} \overset{C·CO_2Et}{\underset{CO}{CH}} \xrightarrow{PCl_5} \underset{N}{\bigodot} \overset{CO_2H}{\underset{Cl}{}}$$

In this case the elimination of the halogen atom remains to be accomplished.[44]

The 2-hydroxy- and 2-phenyl-derivatives of 3-phenylcinchonic acid undergo internal condensation when treated with sulphuric acid.[45]

(I.) $\bigodot$ CO ·   (II.) $\bigodot$-CO-$\bigodot$

OH(or Ph)

As would be expected by analogy with fluorenone, the resulting ketones (I) are yellow, whilst di-2-quinolyl ketone (II), prepared by hydrolysis of the condensation product of nitrosodimethylaniline with diquinolylmethane, is colourless.[46]

Reduction of ethyl 2 : 2'-dinitrodibenzylmalonate furnishes bishydrocarbostyril-3 : 3'-spiran (III), which is interesting owing to the asymmetry of its molecular structure :

(III.) $\bigodot\overset{CH_2—}{\underset{NH·CO}{}}C\overset{CH_2—}{\underset{CO·NH}{}}\bigodot$

(IV.) $\bigodot\overset{CH_2—}{\underset{O·CO}{}}C\overset{CH_2—}{\underset{CO·NH}{}}\bigodot$ (V.) $\bigodot\overset{CH_2—}{\underset{O·CO}{}}C\overset{CH_2—}{\underset{O·CO}{}}\bigodot$

Accordingly, its 6 : 6'-disulphonic acid has been resolved into optically active components by means of the quinine salts. The spiro-compounds (IV) and (V) were also prepared in the course of this investigation.[47]

The constitution previously attributed to the cyanines[48] has

[44] E. Thielepape, Ber., 1922, 55, [B],127; A., i, 271.

[45] Farbw. vorm. Meister, Lucius, & Brüning, D.R.-P. 343322; A., i, 867.

[46] G. Scheibe and G. Schmidt, Ber., 1922, 55, [B], 3157; A., i, 1190.

[47] H. Leuchs and H. v. Katinszky, ibid., 710; H. Leuchs, (Miss) E. Conrad, and H. v. Katinszky, ibid., 2131; A., i, 474, 873.

[48] Compare Ann. Reports, 1920, 17, 121.

been confirmed by a synthesis of pinacyanol from quinaldine ethiodide and ethyl orthoformate in presence of acetic anhydride or zinc chloride :

This reaction, it may be noted, is common to the benzothiazoles and to the dialkylindolenines,[49] in which the ·CH:CH· group of the quinoline nucleus is replaced respectively by :S and :CR$_2$. Further, it has been shown that the absorption curves, whether in neutral or in acid solution, of pinacyanol and of diethyliso-cyanine are almost identical in form. This is a particular case of a valuable generalisation that the absorption curves of compounds, the relationship of which is expressed by the formulæ (I) and (II), are very similar, to an extent increasing with the value of n.

$$\text{(I.)} \quad \text{(H or) } \overset{Ar}{\underset{Alk}{>}}\underset{X}{N}:[CH]_{\overline{2n-1}}N<^{Ar}_{Alk} \text{ (or H)}$$

$$\text{(II.) H or } \overset{Ar}{\underset{Alk}{>}}\underset{X}{N}:[CH]_{\overline{2n-1}}CH:CH·N<^{Ar}_{Alk} \text{ (or H)}$$

The same paper [50] contains a general review of the various types of cyanines, and proposals for a comprehensive system of nomenclature to replace the present somewhat trivial designations, and capable of application to products in which the unsaturated carbon chain between the nuclei is prolonged. Compounds of this type have yet to be prepared, but experiments in this direction will not be lacking in view of the obvious interest attaching to them.

The two dyestuffs, which result from the action of a base, preferably pyridine, on a mixture of the alkyl iodides of benzothiazole and its 1-methyl derivative, correspond in general properties to the cyanines.[51] This similarity extends to their constitution, for the yellow diethylthiocyanine iodide has been synthesised by the reactions indicated :

[49] Compare W. König, *J. pr. Chem.*, 1911, [ii], **84**, 194; *A.*, 1911, i, 808.
[50] W. König, *Ber.*, 1922, **55**, [*B*], 3293; *A.*, i, 1188.
[51] A. W. v. Hofmann, *ibid.*, 1887, **20**, 2262; W. H. Mills, T., 1922, **121**, 455; W. H. Mills and W. T. K. Braunholtz, *ibid.*, 1489.

$$\text{(SH, NH}_2) + CH_2(CO_2Et)_2 + (\text{HS, H}_2N) \rightarrow [\text{C·CH}_2\text{·C}]$$

monoethiodide

+ alkali

(I.) C:CH·C (Et, Et, I) $\leftarrow$ C:CH·C (Et)

The virtual tautomerism observed in the case of the *iso*cyanines recurs in the thiocyanines,[52] for the same methyl diethylthiocyanine iodide (I) is obtained, whether the ethiodides of 5- and 1-methylbenzothiazoles or of 1 : 5-dimethylbenzothiazole and benzothiazole be condensed.

(I.) Me C·CH:C Et I Et

$\dfrac{R}{X}\!\!>\!N$ $CH:C$ N R (II.)

The purple compounds formed simultaneously with the thiocyanines correspond with the carbocyanines, and are formed in a similar manner by the linking up of two molecules of 1-methylbenzothiazole alkyl halide through a methenyl group derived from the benzothiazole alkyl halide. The synthesis of these thiocarbocyanines has been referred to above, although in this case experimental details are not yet available.

Thio*iso*cyanines (II) have been synthesised, and resemble the *iso*cyanines in their general characters.[53]

The indenoquinolines (I) and (II) result from the condensation of *o*-aminopiperonal with α- and β-hydrindones, respectively.[54] The anhydro-base derived from the methosulphate of (II) is purple and therefore is written as (III), the relationship between (II) and (III) being akin to that of the colourless and coloured forms of diquinolylmethane.[55]

[52] Compare *Ann. Reports*, 1920, **17**, 122.
[53] W. T. K. Braunholtz and W. H. Mills, *T.*, 1922, **121**, 2004.
[54] J. W. Armit and R. Robinson, *ibid.*, 827.
[55] Compare *Ann. Reports*, 1921, **18**, 117.

CH CH$_2$

(I.) CH$_2$<^O_O—[structure]

CH

CH$_2$<^O_O—[structure] (II.)

N CH$_2$

(III.) CH$_2$<^O_O—[structure]

The condensation of isatin with α-tetralone (tetrahydro-α-naphthol) in presence of potassium hydroxide is a similar reaction to that just referred to. The product, 3 : 4-dihydro-1 : 2-naphthacridine-14-carboxylic acid (IV), is termed tetrophane to recall its similarity in constitution to atophane (V), but the two differ profoundly in their pharmacological action.[56] The new compound resembles strychnine in its action on the spinal cord.

CO$_2$H
C CH$_2$
[structure] C CH$_2$
C
N

(IV.)

CO$_2$H
[structure]
N

(V.)

NH CO·C$_6$H$_4$·NH$_2$
[structure]
N

(VI.)

When indigotin is boiled with aniline, preferably in presence of a condensing agent, reaction occurs, probably in the normal manner between the carbonyl and the amino-groups :

$$C_{16}H_{10}O_2N_2 + 2C_6H_5 \cdot NH_2 = C_{28}H_{20}N_4 + 2H_2O.$$

The product,[57] which furnishes isatin on oxidation, is rearranged by warm dilute mineral acid to an isomeride, no longer oxidisable to isatin, but which on hydrolysis yields aniline and o-aminobenzoyl-5-quinoline (VI).[58]

A number of 9-aminoacridines have been described, and are found to possess bactericidal properties.[59]

The method of separation of isoquinoline from coal tar quinoline [60] depending on the greater basicity of the former has been improved.[61]

[56] J. v. Braun and P. Wolff, Ber., 1922, **55**, [B], 3675; A., 1923, i, 143.

[57] E. Grandmougin and E. Dessoulavy, ibid., 1909, **42**, 3636, 4401; A., 1909, i, 968; 1910, i, 73.

[58] E. Grandmougin, Compt. rend., 1922, **174**, 1175; A., i, 584.

[59] M. L. B., Brit. Pat. 176038; A., i, 468.

[60] R. Weissgerber, Ber., 1914, **47**, 3175; A., 1915, i, 302.

[61] J. E. G. Harris and (Sir) W. J. Pope, T., 1922, **121**, 1029.

A review of the attempts made to synthesise *iso*quinolines from compounds of the type (I) has led to the conclusion that success is only attained when the compound contains a system of conjugated double bonds, and a hydroxyl or alkyloxy-group in the β-position to the nitrogen atom, or when such a system can be formed in the course of the reaction.[62]

(I)   (II.)   (III.)   (IV.)

It has been shown that 1-, but not 3-, methyl*iso*quinoline contains a reactive methyl group, and that 4-phenyl-2-methyl- (IV), but not 2-phenyl-4-methyl-thiazole is similarly reactive. The difference is attributed either to the direct influence of the double bond between the nitrogen atom and the carbon atom, contiguous to the methyl group, or to the possibility which this confers of the formation of a tautomeride, for example (III).[63]

Alkaloids.

Earlier investigations of ricinine had shown that it responded to the tests for the presence of a glyoxaline ring,[64] contained one methylimino-group,[65] and was broken down by 57 per cent. sulphuric acid into ammonia, carbon dioxide, and a compound, $C_7H_9O_2N$. The presence of a pyridine ring in the alkaloid had previously been suspected,[66] and it has now been shown [67] that the product just mentioned is a pyridone, since it is also obtained by spontaneous loss of methyl iodide from 2 : 4-dimethoxypyridine methiodide (I). Of the two possible formulæ thus indicated, (II) is adopted, because the boiling point of the compound suggests that it is derived from *N*-methyl-2-pyridone rather than from the 4-isomeride, and ricinine is considered to be most probably either (III) or (IV).

[62] P. Staub, *Helv. Chim. Acta*, 1922, **5**, 888; *A.*, 1923, i, 140.

[63] W. H. Mills and J. L. B. Smith, *T.*, 1922, **121**, 2724.

[64] E. Schulze and E. Winterstein, *Z. physiol. Chem.*, 1904, **43**, 211; *A.*, 1905, ii, 112; B. Böttcher, *Ber.*, 1918, **51**, 673; *A.*, 1918, i, 304.

[65] B. Böttcher, *loc. cit.*

[66] L. Maquenne and L. Philippe, *Compt. rend.*, 1904, **138**, 506; **139**, 840; *A.*, 1904, i, 339; 1905, i, 80; B. Böttcher, *loc. cit.*

[67] E. Späth and E. Tschelnitz, *Monatsh.*, 1921, **42**, 251; *A.*, i, 571.

(I.)   (II.)   (III.)   (IV.)

(V.)

Of the four asymmetric carbon atoms in the general formula (V) of the cinchona alkaloids, it is already known [68] that the spatial distribution of the groups respectively attached to (1) and (2) is similar in each of the alkaloids, and dextrorotatory in total effect. Also, the stereoisomerism of cinchonine and cinchonidine, or of quinine and quinidine is conditioned by the different distribution round (3). Attention has now been drawn [69] to the fact that of the four possible reduction products of hydrocinchoninone,[70] the most dextrorotatory is dihydrocinchonine, whilst the most lævo-rotatory is dihydrocinchonidine. If the principle of optical super-position be adopted in a semi-quantitative sense, it follows that in dihydrocinchonine, and hence in cinchonine itself, the effects of (3) and (4) must be both dextrorotatory, whilst in cinchonidine and its dihydro-derivative they are centres of lævorotation. The extension of these conclusions to the other alkaloids is based on a comparison of the rotatory values of the alkaloids, their mono-chloro-derivatives, and their deoxy-derivatives. This indicates that quinine, dihydroquinine, cinchonidine, dihydrocinchonidine, and ethylhydrocupreine (optochin) are alike in configuration, but differ in this respect from quinidine, hydroquinidine, cinchonine, and hydrocinchonine. A conception of the absolute nature of the spatial distribution of the groups round each of the four carbon atoms in question is still lacking, but appears to be deducible if further investigation should confirm the statement [71] that internal ethers, $O{<}^{CHMe}_{-CH}{>}C_{16}H_{17}N_2$, are obtainable from hydroxydihydro-cinchonine but not from hydroxydihydrocinchonidine. For such ether-formation would seem to demand that the $\cdot CH_3\cdot CH(OH)\cdot$

[68] P. Rabe and others, *Annalen*, 1910, **373**, 89; *A.*, 1910, i, 417.
[69] H. King and A. D. Palmer, *T.*, 1922, **121**, 2577.
[70] Compare *Ann. Reports*, 1921, **18**, 140.
[71] Compare *ibid.*, 1920, **17**, 120.

and the ·CH(OH)· groups, respectively attached to (1) and (3), are on the same side of the piperidine ring structure, but on the opposite side to the methylene groups of the quinuclidine bridge.

It need scarcely be pointed out that the asymmetry of the ter-valent nitrogen atom in these alkaloids does not increase the number of isomerides possible, because the spatial distribution of the groups attached to it is not independently variable. This, however, does not apply to the cincho- and quina-toxins, and correspondingly it is found [72] that although the conversion of the toxins prepared from the alkaloids furnishes yields exceeding 80 per cent., these only amount to 50 per cent. when synthetic toxins, presumably composed of a mixture represented by (I) and (II), are employed.

$$\text{(I.)} \quad \overset{|}{\underset{|}{N}}H \quad \overset{|}{\underset{|}{C}}H_2 \quad \longrightarrow \quad \overset{|}{N}-\overset{|}{C}H \quad ; \quad H\overset{|}{N} \quad \overset{|}{C}H_2 \quad \text{(II.)}$$
$$CO- \qquad\qquad CO- \qquad\qquad CO-$$

The quinuclidine nucleus would seem to be in some way responsible for the pneumococcidal properties of the cinchona alkaloids, since neither dihydroquinatoxin nor the corresponding secondary alcohol is as efficient in this respect as dihydroquinine.[73]

A revision of the results of earlier workers has shown that the quinoline nucleus is attacked when dihydrocinchonine is reduced in amyl-alcoholic solution by sodium. The three products isolated —hexahydrocinchonine, together with epimeric α- and β-hexa-hydrodeoxycinchonines—each show the reactions of secondary bases.[74]

On the other hand, it is suggested that the quinuclidine, rather than the quinoline, nucleus is attacked when quinine is converted into an amino-oxide by treatment with hydrogen peroxide. This conclusion is based on the fact that the reaction does not apply to quinoline, but that similar compounds have been obtained from quinidine, dihydrocupreine, and optochin. This argument, how-ever, does not seem very satisfactory, since cinchonine does not react in this manner. Quinine oxide is sufficiently stable to permit of its reduction to dihydroquinine oxide.[75]

The 5-, and, less readily, the 8-amino-groups of 5 : 8-diamino-6-methoxyquinoline are replaced by hydroxyl when the compound is boiled with hydrochloric acid. 5 : 8-Diaminodihydroquinoline

[72] P. Rabe, *Ber.*, 1922, **55**, [*B*], 522; *A.*, i, 361; P. Rabe, K. Kindler, and O. Wagner, *ibid.*, 532; *A.*, i, 361.

[73] M. Heidelberger and W. A. Jacobs, *J. Amer. Chem. Soc.*, 1922, **44**, 1098; *A.*, i, 673.

[74] W. A. Jacobs and M. Heidelberger, *ibid.*, 1079; *A.*, i, 672.

[75] E. Speyer and A. G. Becker, *Ber.*, 1922, **55**, [*B*], 1321; *A.*, i, 674.

reacts still more readily, so that apparently the intermediate hydroxyamino-compound is not isolated. But, on the other hand, 5 : 8-diaminoquinoline is recovered practically unchanged.[76] This favourable influence of the 6-methoxy-group is also observed in the analogous case of the hydrolysis of benzeneazo-5-amino-quinoline.[77]

The position of the methoxy-group in harmine and harmaline has now been conclusively fixed by the reduction of synthetic methoxyketomethyldihydrocarboline (I) (see p. 128) in butyl alcoholic solution by means of sodium to a base, which must be N-methyltetrahydronorharmine (II), since it may be similarly obtained from norharmine methosulphate (III) :

Furthermore, synthetic N-methyltetrahydronorharmine has been oxidised by potassium permanganate in acetone solution to the neutral substance (IV), originally obtained by similar means from harmaline (V), thus confirming the formulæ of these two compounds. The neutral substance has also been reduced to N-methyltetrahydronorharmine.[78]

The oxidation of norharman methosulphate to ketomethyldihydrocarboline is evidence that in the free compound addition of methyl sulphate occurs on the pyridine rather than on the pyrrole nitrogen atom, in agreement with an earlier suggestion [79] that the former was the more basic of the two.

In accordance with the formula (I) previously suggested for rutæcarpine, which accompanies evodiamine in *Evodia rutæcarpa*,[80] the former is almost quantitatively converted by treatment with

[76] W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1922, **44**, 1073; *A.*, i, 671.

[77] *Ann. Reports*, 1921, **18**, 138.

[78] W. O. Kermack, W. H. Perkin, and R. Robinson, *T.*, 1922, **121**, 1872.

[79] W. H. Perkin and R. Robinson, *ibid.*, 1919, **115**, 933.

[80] Y. Asahina and S. Mayeda, *J. Pharm. Soc. Japan*, 1916, No. **416**; *A.* 1921, i, 48; compare *Ann. Reports*, 1921, **18**, 142.

amyl alcohol and potassium hydroxide into 2-β-aminoethylindole-3-carboxylic acid, from which 2-β-aminoethylindole itself is obtained by means of hydrochloric acid : [81]

(I.)

A new isomeride of tropine has been isolated from among the basic residues remaining after removal of ecgonine from the products of hydrolysis of the coca alkaloids, but no constitutional formula has been assigned to it.[82] The hydroecgonidine prepared by catalytic reduction of anhydroecgonine consists of two stereo-isomerides.[83] It would therefore seem that the older formula [84] for anhydroecgonine (I) must be replaced by (II), and this is supported by the observed exalted molecular refraction of the ethyl ester of anhydroecgonine as compared with that of hydroecgonidine.

The formula attributed to scopoline [85] has been revised on interesting stereochemical grounds. It had previously been a matter for comment that whilst not more than two optically active forms of the alkaloid had been obtained,[86] the products of its hydrolysis were each known to contain asymmetric carbon atoms.[87] Further, when the asymmetry of the tropyl residue in the alkaloid was destroyed by converting the latter into *apo*scopolamine (III), the latter could not be resolved :

(III.)

[81] Y. Asahina and A. Fujita, *J. Pharm. Soc Japan*, 1921, 863; *A.*, i, 47.

[82] J. Tröger and K. Schwarzenberg, *Arch. Pharm.*, 1921, **259**, 207; *A.*, i, 167.

[83] J. Gadamer and C. John, *ibid.*, 227, 244; *A.*, 'i, 167, 675.

[84] R. Willstätter and W. Müller, *Ber.*, 1898, **31**, 2655; *A.*, 1899, i, 178.

[85] Compare *Ann. Reports*, 1920, **17**, 127; 1921, **18**, 143.

[86] H. King, *T.*, 1919, **115**, 476, 974; *Ann. Reports*, 1919, **16**, 117.

[87] H. Tutin, *T.*, 1910, **97**, 1793.

Again, the d-phenylpropionate resulting from the reduction of aposcopolamine consisted of only one racemate. When, however, the attempt was made to synthesise the same compound from scopoline and d-phenylpropionyl bromide, the product was composed of two readily separable racemates. The remarkable conclusion was therefore reached that the alcohol of which scopolamine (I) is the ester is probably internally compensated, but suffers a rearrangement, when liberated by hydrolysis, into the asymmetric scopoline (II). These relationships are represented as follows : [88]

$$
\begin{array}{c}
\text{CH}_2\text{-CH--CH}\diagdown \\
\text{CHPh·CO·O·CH} \quad \text{NMe} \quad \Big| \quad \text{O} \\
\text{CH}_2\text{·OH} \qquad \text{CH}_2\text{-CH--CH}\diagup \\
\text{(I.)}
\end{array}
\quad\rightarrow\quad
\begin{array}{c}
\left[\begin{array}{c}
\text{CH}_2\text{-CH--CH·OH} \\
\text{HO·CH} \quad \text{NMe} \quad \Big| \\
\text{CH}_2\text{-CH--CH·OH}
\end{array}\right] \\
{}_{(4)}\qquad {}_{(3)}
\end{array}
\quad\rightarrow
$$

$$
\begin{array}{c}
\text{CH}_2\text{-CH--CH·OH} \\
\text{--CH} \quad \text{NMe} \quad \Big| \\
\text{CH}_2\text{-CH--CH} \\
\text{---O---} \\
\text{(II.)}
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2\text{----CH--CH·OH (2)} \\
{}_{(5)}\ \text{CH·OH} \quad \text{NMe} \quad \Big| \\
{}_{(6)}\ \text{CH}_2\text{----CH--CH·OH (1)} \\
{}^{(7)} \\
\text{(III.)}
\end{array}
$$

The formula thus assigned to scopoline had been previously suggested [89] to account for its conversion into 1 : 2-dihydroxytropane, and for the natural occurrence of scopolamine and tropine in the same plant. In the formula (III) suggested at the same time for teloidine, as a concomitant of the bases just named, the 1- and 5-hydroxyl groups are probably in the trans-position, since the formula (II) for scopoline shows that cis-hydroxyl groups would probably give rise to an oxide ring. A fuller account has also been given of the products obtained by the degradation of scopoline by exhaustive methylation.

The structural relationship so frequently observed between alkaloids which occur together is also well illustrated by the formulæ assigned to five of the seven known cactus alkaloids. Anhaline (I) has been identified with hordenine,[90] whilst mezcaline (II) is known to be β-3 : 4 : 5-trimethoxyphenylethylamine.[91] It has now been shown [92] that N-acetylmezcaline may be converted by the usual means into 6 : 7 : 8-trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, from which by reduction the corresponding

[88] K. Hess and O. Wahl, Ber., 1922, 55, [B], 1979; A., i, 854.

[89] H. King, loc. cit., p. 487.

[90] E. Späth, Monatsh., 1919, 40, 129; 1921, 42, 263; A., 1919, i, 548; 1922, i, 567.

[91] Idem, ibid., 1919, 40, 129; A., 1919, i, 548; compare Ann. Reports, 1919, 16, 123.

[92] Idem, ibid., 1921, 42, 97; A., i, 163.

tetrahydro*iso*quinoline is obtained. This, and its N-methyl derivative, are

(I.)　　　　(II.)　　　　(III.) Me

(IV.) Me　　　　(V.)

respectively identical with the O-methyl derivatives of anhalonidine (III) and pellotine (IV). It therefore only remains to determine which of the three methoxy-groups of the synthetic compounds corresponds with the phenolic hydroxyl in the two alkaloids. The probable mode of attacking this problem is indicated by that successfully adopted in the case of anhalamine (V), and indicated in the following scheme representing the synthesis of this base from gallic acid : [93]

$$C_6H_2(OH)_3 \cdot CO_2H \longrightarrow C_6H_2(CO_2H) \!<\! {(OMe)_2[3:4] \atop OH[5]} \longrightarrow$$

$$C_6H_2(CO_2H) \!<\! {(OMe)_2 \atop O \cdot CO_2Et} \longrightarrow$$

Again, the bases which accompany palmatine in the calumba root, and are separated from it by successively extracting the mixture of the iodides of the bases with potassium carbonate and with potassium hydroxide, are now shown to furnish on methyl-ation products, not only identical with each other, but also with palmitine. The identity also extends to the tetrahydro-bases and therefore it follows that the calumba root contains besides palmatine, phenolic bases having one or more free hydroxyl groups

[93] E. Späth and H. Röder, *Monatsh.*, 1922, **43**, 93; *A.*, i, 852.

in place of methoxyl groups in palmatine, or else phenolic oxygen combined with complexes easily removable by hydrolysis. It should be noted, however, that the homogeneity of the above two basic extracts, columbamine and iatrorhicine, is not quite certain.[94]

The formula previously assigned to laudanine [95] has been confirmed by synthesis.[96] This follows the course now so familiar as to be almost conventional in such cases, and furnishes another illustration (compare the synthesis of anhalamine, above) of the device of masking a phenolic hydroxyl group throughout such a synthesis by its conversion at the outset into an ethylcarbonato-group, from which it can be regenerated at the conclusion.

The need for a revision of the formula of corydaline has been admitted, and (I) is now suggested, since dehydrocorydaline, derived by removal of four hydrogen atoms through the agency of mercuric acetate, is found to undergo the Cannizzaro reaction with sodium hydroxide.[97]

Passing reference has already been made to an investigation of *iso*chondodendrine, in which considerable progress has been made towards the determination of its constitution. But it would seem advisable to defer a fuller account of this until one or two outstanding points have been cleared up by further investigation.

Several papers have appeared on the chemistry of the morphine alkaloids and of strychnine, but these are not of a character which may usefully be dealt with here.

J. KENNER.

[94] E. Späth and K. Böhm, *Ber.*, 1922, **55**, [B], 2985; *A.*, i, 1174.

[95] Compare *Ann. Reports*, 1921, **17**, 144.

[96] E. Späth and N. Lang, *Monatsh.*, 1921, **42**, 273; *A.*, i, 568.

[97] J. Gadamer and F. von Bruckhausen, *Arch. Pharm.*, 1922, **259**, 245; *A.*, i, 675.

ANALYTICAL CHEMISTRY.

THE number of analytical papers now being published has fully reached the standard of the years before the war, and therefore the prefatory remarks to last year's Report are still more applicable to the present Report.

Physical Methods.

The useful process of separating the constituents of minerals by treatment with liquids of different density has been extended by the introduction of three colourless liquids, namely, barium bromomercurate solution, saturated aqueous thallium formate solution, and a mixture of aqueous solutions of thallium formate and malonate. By using these at different temperatures a range of density from 3·1 to more than 5 is obtained.[1]

There have been several new applications of spectroscopy to analytical work. For example, it has been shown that the spectroscope affords the most accurate means of distinguishing between cæsium and rubidium; [2] also, that germanium may be easily identified by its arc spectrum, which shows a characteristic line in the blue region.[3]

In a further development of a research on spectrophotometry [4] it has been found that the method, when used in conjunction with data previously recorded, will enable the proportion of enol in keto-enol mixtures to be estimated with a fair degree of accuracy, provided it is possible to ascertain the optical constants of the respective pure constituents.[5]

By making mixtures of pure argon with pure xenon and with pure krypton, and determining the pressure at which the spectrophotometric intensity of selected lines in the spectra of the respective mixtures becomes equal to that of corresponding selected lines in the argon spectrum, it has been found possible to calculate the proportions of xenon and krypton in the two mixtures.[6]

[1] E. Clerici, *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 116; *A.*, ii, 578.

[2] J. Missenden, *Chem. News*, 1922, **124**, 362; *A.*, ii, 658.

[3] J. Papish, *ibid.*, 3; *A.*, ii, 163.

[4] K. von Auwers and H. Jacobsen, *Annalen*, 1918, **415**, 169; *A.*, 1918, ii, 381.

[5] *Idem, ibid.*, 1922, **426**, 161; *A.*, ii, 168.

[6] C. Moureu and A. Lepape, *Compt. rend.*, 1922, **174**, 908; *A.*, ii, 394.

The difference in the colour reactions of methylfurfuraldehyde and hydroxymethylfurfuraldehyde when converted into phloro-glucides may be sharply distinguished by the use of the ultra-violet spectroscope.[7]

Mention may also be made of a new method of colour measure-ment based upon spectrophotometric measurements.[8]

The more recent work on nephelometry has included a study of the cause of the deviations from the proportionality between the amount of diffracted light and the concentration of coloured sols and turbidities. It is due to the selective absorption of light by the coloured particles, and may be prevented by the use of suitable light filters placed between the source of light and the nephelometer.[9]

A new type of nephelometer has also been devised in which the two fields are made concentric. By using two Nicol prisms, by which the light can be registered and regulated, in place of one of the tube systems in this instrument, a permanent standard may be established.[10]

An optical method of estimating the colloidal portion of tungsten powder has been based on the absorption of light from a quartz-mercury lamp by the solution from which the powder has sedi-mented, and the measurement of the absorption by the deflection of a galvanometer when the light passing through the solution is received on a potassium photo-electric cell.[11]

A new principle of estimating unweighable quantities of metals such as lead or bismuth consists in the use of the radioactive iso-topes of the metals as indicators. Since the active and inactive isotopes, when once mixed, cannot be separated by chemical methods, the detection of the former by means of the electroscope is also an indication of the presence of the latter.[12]

Another application of the electroscopic method of analysis has been its use in the estimation of thorium in monazite sand by means of the emanation. The percentage of thorium-X is calculated from the electroscope readings by means of the formula

$$X = AT_s(T_b - T_u)/T_s(T_b - T_s),$$

where A represents the proportion of thorium in a standard sample, T_s the time of discharge of the electroscope by this standard

[7] J. Tadokoro, *J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 52; *A.*, ii, 236.

[8] H. E. Ives, *J. Opt. Soc. Amer.*, 1921, **5**, 469; *A.*, ii, 221.

[9] H. Bechhold and F. Hebler, *Kolloid Z.*, 1922, **31**, 7; *A.*, ii, 652.

[10] A. A. Weinberg, *Biochem. Z.*, 1921, **125**, 292; *A.*, ii, 309.

[11] A. Lottermoser, *Kolloid Z.*, 1922, **30**, 53; *A.*, ii, 230.

[12] F. Paneth, *Z. angew. Chem.*, 1922, **35**, 549; *A.*, ii, 785.

sample, T_b the time of discharge by a blank sample free from thorium, and T_u by the sample under examination.[13]

A new thermometric method of titrating acids has been devised, *the solution being mechanically stirred in a vacuum tube, while* alkali solution is added at regular intervals in amounts causing the temperature to increase by not more than 0·02°. When the temperature readings are plotted as ordinates and the number of c.c. of alkali as abscissæ, a decided change in the direction of the curve indicates the end-point. The method not only gives results identical with those given by electrometric methods, but also indicates other points at which changes in the nature of the reaction take place.[14]

Gas Analysis.

The most suitable concentration of pyrogallol solution for ab-sorption of oxygen in gas analysis has been ascertained by tabu-lating the absorptive capacities of solutions of all concentrations in a Gibbs triangular diagram for the system pyrogallol, potassium hydroxide, and water. By this means it has been found that the best results are obtained by the use of a solution of 20 parts of pyrogallol and 20 parts of potassium hydroxide in 60 parts of water.[15]

It has also been shown that in using acid cuprous chloride solution as an absorbent for carbon monoxide the rate of absorption and the stability of the reagent are increased by the addition of stannous chloride.[16]

For the accurate estimation of hydrogen in the presence of gaseous paraffins advantage has been taken of its reducing action on palladous chloride, the separated palladium being collected, dried, and weighed, and calculated into the equivalent amount of hydrogen.[17]

Various absorbents have been tried for the estimation of hydrogen phosphide. The gas is completely absorbed by iodic acid solution within thirty minutes, and by distilling the liberated iodine into potassium iodide solution and titrating the liquid it is possible to estimate the phosphine. Or the phosphoric acid in the flask may be estimated as magnesium pyrophosphate. Another method is to absorb the hydrogen phosphide in standard silver nitrate, mer-curic chloride, or gold chloride solution, and to estimate the phos-

[13] H. H. Helmick, *J. Amer. Chem. Soc.*, 1921, **43**, 2003; *A.*, ii, 164.

[14] P. Dutoit and E. Grobet, *J. Chim. physique*, 1922, **19**, 324; *A.*, ii, 578.

[15] F. Hoffmann, *Z. angew. Chem.*, 1922, **35**, 451; *A.*, ii, 582.

[16] A. Kropf, *ibid.*, 451; *A.*, ii, 657.

[17] J. A. Muller and A. Foix, *Bull. Soc. chim.*, 1922, [iv], **33**, 713; *A.*, ii, 655.

phoric acid in the filtrate from the precipitated silver, etc.[18] A special form of absorption apparatus for this process has been devised.[19]

The absorption of carbon dioxide formed in the estimation of minute quantities of methane may be rapidly effected in one vessel by adding gelatin solution to the baryta absorbent, the resulting scum prolonging the contact of the gases with the reagent.[20]

Further particulars have been published of the method of estimating benzene by absorption with charcoal.[21] A correction for the benzene retained by the charcoal is found by means of a control test.[22]

An accurate thermometric method of estimating minute quantities (0·001 to 1 per cent.) of oxygen in hydrogen consists in passing the gas through a platinised catalyst at 305°, and measuring the rise in temperature, caused by the combustion of the hydrogen, by means of a thermo-element connected with a galvanometer.[23]

Another method of estimating traces of oxygen, which is particularly suitable for biochemical work, is to convert the oxygen, by means of nitric oxide and sodium hydroxide, into sodium nitrite, which is then estimated colorimetrically by means of sulphanilic acid and α-naphthylamine.[24]

It has been found that when air is used as the source of oxygen in slow combustion and explosion methods of gas analysis no appreciable error results if the time of burning does not exceed three minutes and the platinum wire is not heated too strongly. Otherwise, an error of as much as 2 per cent. may be caused by the formation of oxides of nitrogen.[25]

When estimating nitrogen peroxide and nitric oxide in gas mixtures by absorption with alkali solutions it is necessary to take into consideration the fact that if a mist has previously developed, owing to chilling of the gas, some of the nitrogen peroxide will have been converted into nitric acid and nitric oxide, and that these constituents must be absorbed and included in the calculations.[26]

Traces of oxides of nitrogen in air may be accurately estimated

[18] L. Moser and A. Brukl, *Z. anorg. Chem.*, 1921, **121**, 73; *A.*, ii, 393.

[19] L. Moser, *ibid.*, 1922, **121**, 313; *A.*, ii, 519.

[20] E. Murmann, *Oesterr. Chem. Ztg.*, 1922, **25**, 90; *A.*, ii, 591.

[21] Compare *Ann. Reports*, 1921, **18**, 149.

[22] E. Berl, *Z. angew. Chem.*, 1922, **35**, 332; *A.*, ii, 591.

[23] A. T. Larson and E. C. White, *J. Amer. Chem. Soc.*, 1922, **44**, 20; *A.*, ii, 311.

[24] H. M. Sheaff, *J. Biol. Chem.*, 1922, **52**, 35; *A.*, ii, 582.

[25] G. W. Jones and W. L. Parker, *J. Ind. Eng. Chem.*, 1921, **13**, 1154; *A.*, ii, 223.

[26] C. L. Burdick, *ibid.*, 1922, **14**, 308; *A.*, ii, 583.

by oxidising them with sodium hydroxide solution and hydrogen peroxide, and estimating the resulting nitrate colorimetrically by the phenoldisulphonic acid method.[27]

Oxidation with hydrogen peroxide (perhydrol) in alkali solution is also the basis of a method of estimating sulphur compounds of all kinds in coal gas,[28] and hydrogen peroxide is recommended as an absorbent for sulphurous acid in air.[29]

In connexion with this branch of analysis, mention may also be made of a process of estimating gases in metals. A special form of apparatus connected with a Toeppler pump is used, and the gases collected from a weighed quantity of the metal are examined spectroscopically and then analysed by the usual methods.[30]

Agricultural Analysis.

Considerable attention has been given to the standardisation of the methods for the mechanical analysis of soils, and a rapid method has been devised in which measured amounts of a suspension of the soil in a 0·025 per cent. sodium carbonate solution are withdrawn at measured intervals and a relationship (expressed graphically) is established between the percentage of soil and the rate of sedimentation.[31] In order to render humus soils suitable for mechanical analysis, it is necessary to destroy the organic matter. This may be conveniently done by heating the soil with hydrogen peroxide.[32]

For the estimation of humus in soils the carbon dioxide present as carbonate is first removed, and the soil then oxidised with sulphuric acid and potassium dichromate, the gases from the oxidation are conducted through copper oxide and lead chromate, and the carbon dioxide is absorbed and weighed.[33]

It has been shown that the use of a carbon factor for calculating the amount of organic matter in a soil is of questionable value, and that, in any case, results closer to the truth will be obtained by taking the relationship of 50 to 52 per cent. of carbon to represent 100 parts of soil, instead of 58 per cent. as at present.[34]

The amount of moisture in soil may be calculated from the

[27] V. C. Allison, W. L. Parker, and G. W. Jones, *U.S. Bureau of Mines, Techn. Paper*, 249; *A.*, ii, 313.

[28] A. Klemmer, *Chem. Ztg.*, 1922, **46**, 79; *A.*, ii, 224.

[29] G. Lambert, *Z. anal. Chem.*, 1922, **61**, 20; *A.*, ii, 390.

[30] H. L. Simons, *Chem. Met. Eng.*, 1922, **27**, 248; *A.*, ii, 719.

[31] G. W. Robinson, *J. Agric. Sci.*, 1922, **12**, 306; *A.*, ii, 888.

[32] *Idem, ibid.*, 287; *A.*, ii, 888.

[33] A. Gehring, *Z. anal. Chem.*, 1922, **61**, 293.

[34] J. W. Read and R. H. Ridgell, *Soil Sci.*, 1922, **13**, 1; *A.*, ii, 540.

measurement, under specified conditions, of the resistance between two carbon electrodes placed in the soil.[35]

A method of estimating the acidity or basicity of a soil, and also the amount of soluble iron or aluminium salts, depends on extracting the soil with alcoholic potassium thiocyanate solution, and titrating the extract with standard alcoholic alkali or acid. The use of logwood enables a colorimetric estimation of aluminium to be made.[36]

Further evidence has been adduced of the untrustworthiness of citric solubility as a criterion of the agricultural value of mineral phosphates, the amounts of extract obtainable varying with the conditions.[37] A modified method of estimating phosphoric acid has been devised, in which the precipitation with ammonium molybdate is effected in the cold, and the precipitate ultimately dried at 120° and weighed. Less variation in composition thus results than in the case of precipitates obtained in the usual way.[38]

In a combined method of estimating total nitrogen, nitric nitrogen, and nitrous nitrogen in fertilisers, the total nitrogen is first estimated after reduction with ferrum redactum ; the nitrites are removed by distillation as methyl esters, the residual nitrates reduced as before, and the ammonia distilled.[39] The digestion with acid in the Kjeldahl flask may be greatly accelerated by the addition of mercurous iodide, which is much more effective than mercury or other mercury salts.[40]

A simple method of overcoming the difficulty of estimating guanidine when guanylcarbamide is present as an impurity is to precipitate the guanidine as picrate from a solution of sodium hydroxide, leaving the guanylcarbamide picrate in solution.[41] The conditions under which triketohydrindene (ninhydrin) can be used as a quantitative colorimetric reagent for the estimation of amino-acid nitrogen have been worked out, and it has been shown that histidine is the only amino-acid which gives a coloration differing slightly from the standard.[42]

Organic Analysis.

Qualitative.—A general reaction enabling fatty acids of the acetic series to be detected has been found in the formation of their

[35] T. Deighton, *J. Agric. Sci.*, 1922, **12**, 207.

[36] R. H. Carr, *J. Ind. Eng. Chem.*, 1921, **13**, 931; *A.*, ii, 172.

[37] J. F. Tocher, *J. Agric. Sci.*, 1922, **12**, 125; *A.*, ii, 525.

[38] A. W. Clark and R. F. Keeler, *J. Assoc. Off. Agric. Chem.*, 1921, **5**, 103; .4., ii, 84.

[39] F. Mach and F. Sindlinger, *Z. angew. Chem.*, 1922, **35**, 473; *A.*, ii, 783.

[40] M. and I. Sborowsky, *Ann. Chim. anal.*, 1922, **4**, 266; *A.*, ii, 783.

[41] A. H. Dodd, *J. Soc. Chem. Ind.*, 1922, **41**, 445T; *A.*, ii, 536.

[42] H. Riffart, *Biochem. Z.*, 1922, **131**, 78; *A.*, ii, 718.

double sodium uranyl salts, which form characteristic micro-crystalline precipitates.[43]

Other microchemical group reagents are iodic acid, which yields distinctive precipitates with alkaloids and organic bases,[44] and picric acid, which, under standard conditions, forms crystalline picrates of different form with vegetable alkaloids.[45] Veronal and other hypnotics derived from barbituric acid form crystalline dixanthyl derivatives of various melting points, whereas other hypnotics do not react in this way with xanthhydrol.[46]

A stable modification of Schiff's reagent for aldehydes has been prepared from rosaniline hydrochloride and sodium hyposulphite. It can be heated to accelerate the reaction with aldehydes.[47]

The phenol test for formaldehyde is not trustworthy when applied to the distillate from oxidised spirits and tinctures. A solution of guaiacol or *apo*morphine in concentrated sulphuric acid gives more definite results. The former reagent gives a dark red coloration with formaldehyde, and the latter a distinctive precipitate.[48]

The well-known colour reaction of liver oils with sulphuric acid has been shown to stand in some relationship to the vitamin content of the oil, and the test has been applied quantitatively by a method of dilution until the colour is no longer produced.[49] Liquid paraffin (B.P.) is a suitable diluting agent for this purpose.[50]

A new test for carbohydrates has been based on the formation of acetal, identified by its blue fluorescence and by the formation of 3-hydroxy-2-methylquinoline. The acetal reaction is given by all the common sugars and by dextrin, but not by glycerol, starch, or glycogen.[51]

When sucrose is boiled with a saturated solution of ammonium nickel sulphate and a few drops of sulphuric or hydrochloric acid, it gives a distinctive red coloration.[52] Another test for sucrose in the presence of dextrose has been based upon the fact that the

[43] J. Barlot and (Mlle) M. T. Brenet, *Compt. rend.*, 1922, **174**, 114; *A.*, ii, 167.

[44] L. Rosenthaler, *Schweiz Apoth. Ztg.*, 1921, **59**, 477; *A.*, ii, 327.

[45] B. E. Nelson and H. A. Leonard, *J. Amer. Chem. Soc.*, 1922, **44**, 369; *A.*, ii, 327.

[46] R. Fabre, *J. Pharm. Chim.*, 1922, [vi], **26**, 241; *A.*, ii, 795.

[47] E. Wertheim, *J. Amer. Chem. Soc.*, 1922, **44**, 1834; *A.*, ii, 793.

[48] B. Peyl, G. Reif, and A. Hanner, *Chem. Ztg.*, 1921, **45**, 1220; *A.*, ii, 94.

[49] J. C. Drummond and A. F. Watson, *Analyst*, 1922, **47**, 341; *A.*, ii, 665.

[50] H. D. Richmond and E. H. England, *ibid.*, 431; *A.*, ii, 792.

[51] O. Baudisch and H. J. Deuel, *J. Amer. Chem. Soc.*, 1922, **44**, 1585; *A.*, ii, 664.

[52] F. Krys, *Oesterr. Chem. Ztg.*, 1921, **24**, 141; *A.*, ii, 233.

former is soluble and the latter insoluble, in hot ethyl acetate.[53] Lævulose may be detected in the presence of aldoses by the fact that, after treatment with iodine solution and then with sodium hydroxide, it gives a red coloration with Fehling's solution within four minutes, whilst dextrose does not react until after five minutes' heating.[54]

An acidified solution of benzidine hydrochloride gives an orange coloration with ligneous tissue, and since starch can be stained with iodine in the same section, the reagent will be of value in biochemical work.[55]

In this connexion mention should also be made of a qualitative test for tannin based on its fixation on gold-beater's skin, which can then be stained with dilute ferric chloride solution.[56]

An acidified solution of p-nitroaniline hydrochloride, decolorised with sodium nitrite, has been found to be a sensitive reagent for phenols, which, when treated with it and with excess of sodium hydroxide, give colorations ranging from salmon pink to ruby-red, according to the quantity of phenol present. The test will detect 1 part of ordinary phenol in 1,000,000.[57]

A method of distinguishing between phenacetin and acetanilide depends on the difference in the colorations given by the two substances when hydrolysed with sulphuric acid and oxidised with potassium dichromate.[58]

Traces of pyridine may be detected by the formation of a red, crystalline compound, 1-anilinodihydropyridinium phenyl bromide, on treatment with aniline in the presence of water and cyanogen bromide.[59] The test is capable of detecting 1 part of pyridine in 350,000 parts of water.[60]

A new method of estimating the pyrimidine, thymine, has been based on its oxidation into carbamide, acetylcarbinol, and pyruvic acid, and identification of the pyruvic acid by converting it into indigotin.[61]

Quantitative.—There have been several contributions to the method of ultimate analysis. Thus it has been shown that in the wet combustion of organic compounds good results are obtained

[53] L. A. Congdon and C. R. Steward, *J. Ind. Eng. Chem.*, 1921, **13**, 1143; *A.*, ii, 233.

[54] I. M. Kolthoff, *Chem. Weekblad*, 1922, **19**, 1; *A.*, ii, 166.

[55] C. van Zijp, *Pharm. Weekblad*, 1921, **58**, 1539; *A.*, ii, 94.

[56] E. Atkinson and E. O Hazleton, *Biochem. J.*, 1922, **16**, 516; *A.*, ii, 793.

[57] J. Moir, *J. S. African Chem. Inst.*, 1922, **5**, 8; *A.*, ii, 321.

[58] L. Ekkert, *Pharm. Zentr.-h.*, 1921, **62**, 735; *A.*, ii, 169.

[59] A. Goris and A. Larsonneau, *Bull. Soc. Pharmacol.*, 1921, **28**, 497; *A.*, ii, 795.

[60] F. Lehner, *Chem. Ztg.*, 1922, **46**, 877; *A.*, ii, 795.

[61] A. Baudisch and T. B. Johnson, *Ber.*, 1922, **55**, [B], 18; *A.*, ii, 238.

by the use of a mixture of silver chromate and sulphuric acid as the oxidising agent.[62] The method has its drawbacks, however, for it is only applicable to certain types of compounds, such as sugars not containing a methyl group attached directly to a carbon group.[63] The oxidising action of the sulpho-chromic mixture may be increased by the addition of chromic oxide, and the scope of the method thus extended.[64]

A volumetric method of estimating carbon and hydrogen is to pass the gaseous products of the combustion first over a substance, such as chloronaphthyloxychlorophosphine, which yields hydrogen chloride on hydrolysis, and then into standard baryta solution, which is afterwards titrated with standard hydrochloric acid. The carbon dioxide is then removed from the baryta solution after addition of excess of acid, and the residual solution again titrated, this time with standard baryta solution.[65]

For the direct estimation of oxygen the organic substance is heated in a current of hydrogen, and the water formed in the hydrogenation collected and weighed. The method is unsuitable for nitrogen compounds, which yield ammonia on hydrogenation.[66]

A rapid method of estimating chlorine consists in absorbing the products of combustion in water and titrating the absorbed chloride with a mercuric salt, with the use of sodium nitroprusside as indicator.[67]

The low results obtained by the Knecht-Hibbert method of reduction in the estimation of the nitro-groups in certain aromatic compounds has been shown to be due to chlorination reactions. The difficulty can be overcome by using titanous sulphate instead of titanous chloride for the reduction.[68]

Nessler's reagent may be used, not only for the characterisation of aldehydes and ketones, but also for the estimation of certain aldehydes, the iodine liberated in the reaction being titrated with thiosulphate.[69] Another method which is applicable to various aldehydes and ketones is based on the hydroxylamine method [70] of estimating citral.[71]

[62] L. J. Simon, *Compt. rend.*, 1922, **174**, 1706; *A.*, ii, 593.

[63] L. J. Simon and A. J. A. Guillaumin, *ibid.*, **175**, 525; *A.*, ii, 867.

[64] L. J. Simon, *ibid.*, 768; *A.*, ii, 868.

[65] J. Lindner, *Ber.*, 1922, **55**, [*B*], 2025; *A.*, ii, 657.

[66] R. ter Meulen, *Rec. trav. chim.*, 1922, **41**, 509; *A.*, ii, 717.

[67] E. Votoček, *Chem. Listy*, 1922, **16**, 248; *A.*, ii, 863.

[68] T. Callan and J. A. R. Henderson, *J. Soc. Chem. Ind.*, 1922, **41**, 157T; *A.*, ii, 524.

[69] J. Bougault and R. Gros, *J. Pharm. Chim.*, 1922, **26**, 5; *A.*, ii, 666.

[70] A. H. Bennett, *Analyst*, 1909, **34**, 12; *A.*, 1909, ii, 192.

[71] A. H. Bennett and F. K. Donovan, *ibid.*, 1922, **47**, 146; *A.*, ii, 535.

A direct method of estimating acetaldehyde is to treat the solution with excess of an alkaline ammoniacal silver solution and to titrate the reduced silver with ammonium thiocyanate solution.[72] A rapid colorimetric method has also been based on the fact that acetaldehyde gives a yellow coloration with benzidine hydrochloride.[73] An analogous method for estimating furfuraldehyde depends on the coloration which it gives with orcinol.[74]

The conditions affecting the quantitative estimation of reducing sugars by means of Fehling's solution have been studied and means for avoiding some of the errors in the current methods have been devised.[75] It has been found that sucrose is slowly hydrolysed by Fehling's solution to an extent depending on the conditions, and that a blank estimation should therefore be made.[76]

A new method of estimating sucrose consists in heating the sugar with lime and water at 60—80°, and polarising the solution, in which sugars other than sucrose will have been destroyed.[77] The use of invertase for the estimation of sucrose has also been recommended.[78] Numerous errors are involved in the estimation of sugar in urine by fermentation with yeast. They may be reduced to some extent by sterilisation and precipitation of carbonates in the urine with calcium chloride.[79]

The estimation of anthraquinone by the method of Lewis [80] involves certain filtration difficulties; these may be avoided by using a volumetric method of estimation.[81]

A gravimetric method of estimating phenanthrene is based on its oxidation by means of iodic acid to phenanthraquinone, which is then precipitated as toluphenanthrazine by means of 3 : 4-tolylenediamine.[82]

A critical survey of the various methods of estimating alkaloids has been made and the conclusion drawn that, of the gravimetric methods, only precipitation with picric acid, phosphotungstic or silicotungstic acid or with picrolonic acid gives serviceable results, whilst of the volumetric methods titration with standard acid is

[72] W. Stepp and R. Fricke, Z. physiol. Chem., 1921, 116, 293; A., ii, 236.

[73] N. K. Smitt, Bull. Bur. Bio-Techn., 1922, No. 5, 117; A., ii, 402.

[74] P. Fleury and G. Poirot, J. Pharm. Chim., 1922, [vii], 26, 87; A., ii, 666.

[75] F. A. Quisumbing and A. W. Thomas, J. Amer. Chem. Soc., 1921, 43, 1503; A., ii, 92.

[76] E. Canals, Bull. Soc. chim., 1922, [iv], 31, 583; A., ii, 592.

[77] A. Behre and A. Düring, Z. Unters. Nahr. Genussm., 1922, 44, 65; A., ii, 790.

[78] T. S. Harding, Sugar, 1921, 23, 546; A., ii, 167.

[79] C. Lange, Berlin Klin. Woch., 1921, 58, 957; A., ii, 93.

[80] H. F. Lewis, J. Ind. Eng. Chem., 1918, 10, 425; A., 1918, ii, 338.

[81] O. A. Nelson and C. E. Senseman, ibid., 1922, 14, 956; A., ii, 882.

[82] A. G. Williams, J. Amer. Chem. Soc., 1921, 43, 1911; A., ii, 90.

the most trustworthy.[83] Caffeine gives an insoluble precipitate with silicotungstic acid and may be added to the list of alkaloids which can be estimated by means of that reagent.[84]

New methods of estimating morphine, codeine, and narcotine in Indian opium have been described,[85] and a method of estimating meconic acid in opium, based on its separation as calcium meconate.[86]

Considerable attention has been given to the estimation of uric acid, and various modifications and colorimetric methods have been suggested, including one in which an arsenotungstic acid reagent is used [87] in place of the original phosphotungstic acid reagent of Folin and Denis.[88]

Inorganic Analysis.

Qualitative.—A scheme for separating metals by the use of sodium sulphide instead of hydrogen sulphide has been devised, the reagent being added to the hydrochloric acid solution, which has previously been neutralised with sodium carbonate and boiled with dilute sodium hydroxide solution. The resulting precipitate may contain the sulphides, hydroxides, and carbonates of one group of metals, and the filtrate the sulphides of another group.[89] In another scheme of separation no sulphur compounds are used, but nascent hydrogen is produced, as in the Marsh test, in the hydrochloric acid solution. A group, which may contain silver, mercury, lead, bismuth, copper, cadmium, platinum, gold, tin, antimony, and arsenic, is thus precipitated.[90]

A new reagent for microchemical analysis has been found in cæsium chloride, which forms characteristic double chlorides with a large number of metals.[91]

Another sensitive reagent, giving distinctive colorations with certain metals, is a mixture of resorcinol solution and ammonia.[92]

In addition to these group reagents, several useful tests for individual anions have been published. For example, the Kastle-Meyer reagent (an alkaline solution of phenolphthalein decolorised

[83] P. Herzig, *Arch. Pharm.*, 1922, **259**, 249; *A.*, ii, 538.

[84] A. Azadian, *Bull. Soc. chim. Belg.*, 1922, **31**, 15; *A.*, ii, 237.

[85] J. K. Rakshit, *Analyst*, 1921, **46**, 481; *A.*, ii, 96.

[86] H. E. Annett and M. N. Bose, *ibid.*, 1922, **47**, 387; *A.*, ii, 791.

[87] J. L. Morris and A. G. Macleod, *J. Biol. Chem.*, 1922, **50**, 55; *A.*, ii, 328.

[88] O. Folin and W. Denis, *ibid.*, 1913, **13**, 469; *A.*, 1913, ii, 162.

[89] G. Vortmann, *Boll. Sci. Tech.*, **3**, [No. 5]; *A.*, ii, 653.

[90] V. Macri, *Boll. Chim. farm.*, 1922, **61**, 417; *A.*, ii, 779.

[91] H. Ducloux, *Anal. Asoc. Quím. Argentina*, 1921, **9**, 215; *A.*, ii, 77.

[92] Lavoye, *J. Pharm. Belg.*, 1921, **3**, 889; *A.*, ii, 779.

by boiling with zinc powder) gives a pink coloration with a solution containing 1 part of copper in 100 millions.[93]

Bettendorff's test for arsenic (reduction with stannous chloride and hydrochloric acid), when applied as a microchemical test, is ten times as sensitive as the Marsh test; [94] and a solution of potassium thiocyanate will detect 1 part of osmium per million when shaken with the solution of the osmium salt and with ether, the ethereal layer assuming a blue coloration.[95]

A microchemical test for tungsten has been based on the formation of crystals of ammonium paratungstate when tungstic acid is treated with strong ammonia solution.[96]

For the detection of traces of uranium advantage has been taken of the fact that on treating a nitric acid solution of the metal with an excess of granulated zinc, a yellow deposit, apparently $UO_3,2H_2O$, is formed on the zinc.[97]

A reaction enabling magnesium to be separated from phosphate in an ammoniacal solution consists in the formation of the yellow insoluble compound, $(C_9H_6ON)_2Mg,4H_2O$, on treating a suspension of magnesium hydroxide with an aqueous solution of 8-hydroxyquinoline sulphate. The precipitate, which forms characteristic micro-crystals, is given by a solution of 1 part of magnesium in 25,000.[98]

The sensitiveness of the various tests for strontium has been studied, and it has been found that the reaction with sulphuric acid is capable of detecting the smallest amount (1 : 125,000), the addition of alcohol increasing the sensitiveness to 1 : 1,400,000.[99]

Only a few new tests for kations have been published. These include one for fluorine, which consists in the formation of oily drops when the substance is heated at 90° with sand and sulphuric acid in a test-tube.[1]

Quantitative.—Numerous contributions have been published on the methods of determining hydrogen-ion concentration, and in particular on the applicability of various coloured indicators. The wide range, both in the acid and alkaline directions, of xylenol-blue recommends it as preferable to thymol-blue for chemical and biochemical work.[2] Phenol-red, on the other hand, is too

[93] P. Thomas and G. Carpentier, *Compt. rend.*, 1921, **173**, 1082; *A.*, ii, 86.

[94] H. Schencher, *Monatsh.*, 1921, **42**, 411; *A.*, ii, 526.

[95] M. Hirsch, *Chem. Ztg.*, 1922, **46**, 390; *A.*, ii, 459.

[96] J. A. M. van Liempt, *Z. anorg. Chem.*, 1922, **122**, 236; *A.*, ii, 787.

[97] H. D. Buell, *J. Ind. Eng. Chem.*, 1922, **14**, 593; *A.*, ii, 590.

[98] C. T. Mörner, *Pharm. Zentr.-h.*, 1922, **63**, 399; *A.*, ii, 659.

[99] O. Lutz, *Z. anal. Chem.*, 1921, **60**, 433; *A.*, ii, 227.

[1] B. Fetkenheuer, *Wiss. Veröfft. Siemens-Konzern*, 1922, **1**, [3], 177; *A.*, ii, 655.

[2] A. Cohen, *Biochem. J.*, 1922, **16**, 31; *A.*, ii, 387.

greatly affected by the proportion of salts in the liquid to be a suitable indicator under all conditions.[3]   In the case of sodium chloride and potassium chloride the corrections to be applied for a wide range of proportions of either salt have been ascertained for a number of indicators.[4]

By using mixtures of coloured salts (for example, ferric chloride and cobalt nitrate) in certain proportions as standards for the comparison of the colorations obtained with standard indicators, it is possible to determine the hydrogen-ion concentration without the use of buffer solutions.[5]

Greater accuracy is obtainable by the use of mixed indicators and titrating the liquid to a definite tint than is possible by taking the first colour change as the end-point of the titration.[6]   An extended series of such mixed indicators, some of which are particularly suitable for use with coloured liquids, has been drawn up.[7]

In connexion with this part of the subject it may be mentioned that symmetrical diphenylguanidine has been suggested as an ideal acidimetric standard.[8]

A new acidimetric method of estimating copper depends on its precipitation as the salt, $CuSO_4,4NH_3$, by means of alcohol, and titration of a solution of the precipitated salt with standard acid.[9]

Several new oxidimetric methods have been described.   Thus, a rapid method of estimating chromium in nickel-chromium steel is based on its oxidation with potassium permanganate in sulphuric acid solution.[10]

A convenient method of estimating chlorine-ion in the presence of iodine-ion consists in precipitating them as silver salts and treating the precipitate with a measured excess of standard potassium ferrocyanide solution.   This reacts only with the silver chloride, forming an insoluble silver potassium ferrocyanide, which is filtered off, and the excess of ferrocyanide titrated with permanganate.[10]

An oxidation method of estimating sulphides depends on the interaction of sodium sulphide and ferric sulphate and titration of the resulting ferrous sulphate with permanganate after neutral-

[3] A. Massink, *Pharm. Weekblad*, 1921, **58**, 1133; *A.*, ii, 307.

[4] I. M. Kolthoff, *Rec. trav. chim.*, 1922, **41**, 54; *A.*, ii, 222.

[5] *Idem, Pharm. Weekblad*, 1922, **59**, 104; *A.*, ii, 222.

[6] J. L. Lizius and N. Evers, *Analyst*, 1922, **47**, 331; *A.*, ii, 654.

[7] A. Cohen, *J. Amer. Chem. Soc.*, 1922, **44**, 1851; *A.*, ii, 780.

[8] C. A. Carlton, *ibid.*, 1469; *A.*, ii, 654.

[9] S. Minovici and A. Jonescu, *Bul. Soc. Chim. Română*, 1921, **3**, 89; *A.*, ii, 162.

[10] G. B. Bonino, *Gazzetta*, 1921, **51**, ii, 261; *A.*, ii, 78.

isation with alkali carbonate.[11]   In another oxidation method the sulphide is converted into sulphate by means of alkaline sodium hypobromite, the excess of which is estimated iodometrically.[12]

Dithionates resist the action of cold alkaline oxidising agents, and so may be differentiated from most other sulphur salts.   They are decomposed, however, when heated with acid, and a method of estimating them is based on conducting the resulting sulphur dioxide into iodine solution.[13]

A solution of a bromate in strong hydrochloric acid will effect the quantitative oxidation of hydroxylamine and hydrazine, and the excess of bromate may be titrated.   By then measuring the volume of nitrogen liberated from the hydrazine, the two substances can be estimated in the presence of each other.[14]

Further methods involving the use of cadmium as a reducing agent have been described.[15]   For example, uranyl salts may be estimated by reduction with cadmium to uranous salts, followed by titration of the solution with permanganate.   Vanadic acid is alsô quantitatively reduced.[16]   In like manner, chlorates can be reduced to chlorides, and columbium estimated by reduction in a cadmium tube in the presence of ammonium molybdate or vanadate or of titanium sulphate, and subsequent titration with permanganate.[17]

Analogous use of liquid amalgams of cadmium and of zinc have also been described.[18]   These can be used for the volumetric estimation of molybdenum, uranium, etc.,[19] for the reduction and differential titration of solutions containing two metals such as iron, titanium, or uranium, and for the estimation of chloric, bromic, and iodic acids.[20]

Metallic mercury is a suitable reducing agent for estimating vanadic acid in the presence of uranic and arsenic acids, which are not reduced by mercury.[21]

[11] P. P. Budnikoff and K. E. Krause, *Z. anorg. Chem.*, 1922, **122**, 171; *A.*, ii, 782.

[12] H. H. Willard and W. E. Cake, *J. Amer. Chem. Soc.*, 1921, **43**, 1610; *A.*, ii, 80.

[13] A. Fischer and W. Classen, *Z. angew. Chem.*, 1922, **35**, 198; *A.*, ii, 453.

[14] A. Kurtenacher and J. Wagner, *Z. anorg. Chem.*, 1921, **120**, 261; *A.*, ii, 312.

[15] Compare *Ann. Reports*, 1921, **18**, 158.

[16] W. D. Treadwell [with M. Blumenthal and with M. Hooft], *Helv. Chim. Acta*, 1922, **5**, 732; *A.*, ii, 788.

[17] W. D. Treadwell and others, *ibid.*, 806; *A.*, ii, 780.

[18] N. Kanô, *J. Chem. Soc. Japan*, 1922, **43**, 173; *A.*, ii, 519.

[19] *Idem, ibid.*, 333; *A.*, ii, 529.

[20] *Idem, ibid.*, 544; *A.*, ii, 721.

[21] L. R. W. McCay and W. T. Anderson, *J. Amer. Chem. Soc.*, 1922, **44**, 1018; *A.*, ii, 530.

The use of potassium ferricyanide has been shown to give accurate results in the standardisation of thiosulphate solutions for iodometry.[22] A new iodometric method of estimating copper has been based on the oxidation of a cuprous salt with iodine, the excess of which is afterwards titrated. The copper is first converted into cuprous thiocyanate.[23] Hydrogen peroxide or nitric acid cannot be used for the oxidation of cuprous copper in presence of ferrous iron, and in such cases it is best to precipitate the iron from a hot ammoniacal solution by means of a current of air, and to use the filtrate, after removal of the ammonia, for the iodometric estimation of the copper.[24]

The influence of atmospheric oxygen in liberating iodine from hydriodic acid leads to erroneous results in the iodometric estimation of arsenic acid. It may be prevented by adding sodium hydrogen carbonate before the potassium iodide, and having only a minimum amount of hydrochloric or sulphuric acid present.[25]

Good results are obtained in the estimation of arsenic or antimony sulphide by treating their sodium hydroxide solution with iodine solution containing acetic acid and sodium acetate, and titrating the excess of iodine. Atmospheric oxidation is sufficiently checked by the addition of a small amount of gelatin.[26]

When a sulphur compound is heated with powdered iron in the absence of air, the whole of the sulphur is liberated as hydrogen sulphide, which may be collected in zinc sulphide solution and estimated iodometrically.[27]

Several new colorimetric methods have been devised. These include a method of estimating colloidal gold,[28] of estimating vanadium in steel by means of the coloration given by vanadium pentoxide with hydrogen peroxide,[29] of estimating manganese in steel and ores by oxidising it to the compound H_2MnO_3, an alkaline solution of which is yellowish-brown,[30] and of estimating antimony in copper.[31]

A colorimetric method of estimating phosphorus in steels is based on the blue coloration given by a hot solution of thiosulphate with ammonium phosphomolybdate,[32] and another method for phos-

[22] I. M. Kolthoff, *Pharm. Weekblad*, 1922, **59**, 66; *A.*, ii, 224.

[23] R. Lang, *Z. anorg. Chem.*, 1921, **120**, 181; *A.*, ii, 318.

[24] A. Wöber, *Z. angew. Chem.*, 1922, **35**, 336; *A.*, ii, 588.

[25] L. Rosenthaler, *Z. anal. Chem.*, 1922, **61**, 222; *A.*, ii, 584.

[26] F. Nikolai, *ibid.*, 257; *A.*, ii, 585.

[27] L. Losana, *Giorn. Chim. Ind. Appl.*, 1922, **4**, 204; *A.*, ii, 582.

[28] J. A. Muller and A. Foix, *Bull. Soc. chim.*, 1922, [iv], **33**, 717; *A.*, ii, 662.

[29] A. Kropf, *Z. angew. Chem.*, 1922, **35**, 366; *A.*, ii, 590.

[30] J. Heslinga, *Chem. Weekblad*, 1922, **19**, 302; *A.*, ii, 660.

[31] B. S. Evans, *Analyst*, 1922, **47**, 1; *A.*, ii, 231.

[32] L. Losana, *Giorn. Chim. Ind. Appl.*, 1922, **4**, 60; *A.*, ii, 392.

phorus on the coloration given by phosphates when boiled with ammonium vanadate and treated with ammonium molybdate.[33]

In separating arsenic from tungsten by volatilisation in a current of air at 100°, adsorption of arsenic trichloride may be prevented by bringing the tungstic acid into the disperse condition by treatment with pyrogallol (which is subsequently removed), or by adding glacial acetic acid prior to the addition of the hydrochloric acid and methyl alcohol.[34] Hydrolysis of the arsenic trichloride may be remedied by the addition of a salt, such as potassium bromide, which is readily soluble in water but dissolves with difficulty in strong hydrochloric acid. Successive small additions of concentrated hydrochloric acid will also prevent the hydrolysis.[35] In the presence of nitrites and nitrates the distillation method of estimating arsenic may give erroneous results, owing to the formation of nitrosyl chloride. This may be prevented by using hydrazine sulphate with sodium bromide as the reducing agent, and so simultaneously reducing nitrates, etc., to nitrogen.[36]

Minute quantities of arsenic may be quantitatively separated from germanium by treating the solution with a large excess of hydrofluoric acid prior to precipitation with hydrogen sulphide. Fluorogermanic acid is formed and is not precipitated by hydrogen sulphide.[37]

A quantitative estimation of manganese has been based on its precipitation as manganous iodate, which is dried at 100° and weighed.[38]

Selenium oxychloride has been used as a reagent for the separation of columbium and tantalum,[39] and for the separation of molybdenum trioxide from tungsten trioxide.[40]

Another method of separating small amounts of molybdenum from tungsten is to convert the molybdenum into xanthate, which can then be extracted with hot chloroform.[41]

Aluminium can be separated from iron by means of o-phenetidine, but the iron must be in the ferrous condition, since ferric salts give a precipitate with the reagent.[42]

[33] G. Misson, *Bull. Soc. chim. Belg.*, 1922, **31**, 222; *A.*, ii, 78.

[34] L. Moser and J. Ehrlich, *Ber.*, 1922, **55**, [*B*], 430; *A.*, ii, 314.

[35] *Idem, ibid.*, 437; *A.*, ii, 316.

[36] J. J. T. Graham and C. M. Smith, *J. Ind. Eng. Chem.*, 1922, **14**, 207; *A.*, ii, 314.

[37] J. H. Müller, *J. Amer. Chem. Soc.*, 1921, **43**, 2549; *A.*, ii, 320.

[38] S. Minovici and C. Kollo, *Chim. et Ind.*, 1922, **8**, 499; *A.*, ii, 787.

[39] H. B. Merrill, *J. Amer. Chem. Soc.*, 1921, **43**, 2378; *A.*, ii, 230.

[40] *Idem, ibid.*, 2383; *A.*, ii, 229.

[41] D. Hall, *ibid.*, 1922, **44**, 1462; *A.*, ii, 660.

[42] K. Chalupny and K. Breisch, *Z. angew. Chem.*, 1922, **35**, 263; *A.*, ii, 588.

A suitable method of estimating uranium has been based on its extraction from the mineral by means of a mixture of glacial acetic acid and nitric acid.[43]

Electrochemical Analysis.

Among the apparatus for electrometric titration devised during the year mention may be made of a continuous-reading apparatus for the determination of hydrogen-ion concentration,[44] and of an apparatus in which the electrode vessel is attached to a rotating stirrer and carries a small bulb suitable for the preparation of a calomel electrode.[45]

It has been shown that errors in the conductometric method of precipitation are mainly due to excessive solubility of the precipitate, to the precipitate not being constant in composition, and to errors in determining the conductivity; and means of avoiding these errors have been pointed out.[46]

A simple method of electrometric titration for acidimetry or alkalimetry consists in the use of a number of constant and reproducible electrodes which are equivalent to hydrogen electrodes. These are especially useful when it is required to titrate a solution to an end-point of definite hydrogen-ion concentration.[47]

The use of a silver cathode with an anode of platinum alloyed with iridium or rhodium has been recommended for the rapid deposition of copper and zinc under specified conditions, and lead may be deposited as peroxide on the anode or as metal on the cathode according to the conditions of electrolysis.[48]

An iodine electrode may be conveniently used in numerous potentiometric estimations, such as the titration of iodides with silver nitrate, and the analysis of mercuric chloride, thallous salts, etc., but it is unsuitable for the estimation of lead or bismuth.[49] In most cases the end-point of a titration with silver nitrate is indicated by the solubility of the silver compound, and the method gives good results with chlorides, bromides, iodides, and many other salts.[50]

The use of lead nitrate in electrometric titration gives accurate results with iodides in the presence of chlorides and bromides, and for the estimation of certain organic salts.[51]

[43] W. W. Scott, *J. Ind. Eng. Chem.*, 1922, **14**, 531; *A.*, ii, 788.

[44] H. Goode, *J. Amer. Chem. Soc.*, 1922, **44**, 26; *A.*, ii, 307.

[45] C. A. Waters, *J. Soc. Chem. Ind.*, 1922, **41**, 337T; *A.*, ii, 862.

[46] I. M. Kolthoff, *Z. anal. Chem.*, 1922, **61**, 171; *A.*, ii, 452.

[47] P. F. Sharp and F. H. MacDougall, *J. Amer. Chem. Soc.*, 1922, **44**, 1193; *A.*, ii, 579.

[48] A. Kling and A. Lassieur, *Ann. Chim. Analyt.*, 1922, **4**, 171; *A.*, ii, 587.

[49] I. M. Kolthoff, *Rec. trav. chim.*, 1922, *41*, 172; *A.*, ii, 388.

[50] *Idem*, *Z. anal. Chem.*, 1922, **61**, 229; *A.*, ii, 581.

[51] *Idem*, *ibid.*, 369; *A.*, ii, 781.

Halogen-ions may also be accurately titrated with mercuric perchlorate, but only separately and not in admixture.[52]

When titrating ferrocyanides in acid solution with potassium permanganate solution, the end-point may be sharply obtained by an electrometric method,[53] but it is essential that sufficient acid, preferably hydrochloric acid, should be present to prevent the precipitation of manganese ferrocyanide.[54] On the other hand, when using ferrocyanide for the titration of certain metals, such as cadmium, zinc, or lead, the sharpness of the end-point is affected both by the insolubility of the resulting ferrocyanide of the heavy metal and by the nature of the alkali metal present.[55]

In the electrometric estimation of uranium by oxidimetric titration of the reduced uranium salt it is necessary to take into account that there are two changes in the oxidation potential, the first corresponding with the formation of quadrivalent, and the second with that of sexavalent uranium.[56]

An amalgam of zinc gives good results in the reduction of compounds of metals such as iron, molybdenum, vanadium, and uranium, prior to electrometric titration with potassium permanganate solution.[57] Another oxidimetric method consists in reducing a cupric salt with titanium trichloride and subsequently titrating the cuprous salt with standard dichromate or potassium bromate solution in an atmosphere of carbon dioxide.[58]

A series of test experiments has shown that traces of sulphate may be . accurately estimated by conductometric titration with barium chloride, the addition of alcohol being an advantage.[59]

The conductometric method has also been applied to the titration of solutions of hydrofluosilicic acid,[60] to the titration of acids and phenol in alcoholic solution by means of an alcoholic solution of sodium ethoxide,[61] and to the titration of azo-dyestuffs and nitro-compounds.[62]

C. AINSWORTH MITCHELL.

[52] I. M. Kolthoff, *Z. anal. Chem.*, 1922, **61**, 332; *A.*, ii, 665.

[53] E. Müller and H. Lauterbach, *Z. anal. Chem.*, 1922, **61**, 398; *A.*, ii, 795.

[54] I. M. Kolthoff, *Rec. trav. chim.*, 1922, **41**, 343; *A.*, ii, 537.

[55] W. D. Treadwell and D. Chervet, *Helv. Chim. Acta*, 1922, **5**, 633; *A.*, ii, 786.

[56] D. T. Ewing and E. F. Eldridge, *J. Amer. Chem. Soc.*, 1922, **44**, 1484; *A.*, ii, 661.

[57] N. Kanô, *J. Chem. Soc. Japan*, 1922, **43**, 550; *A.*, ii, 721.

[58] E. Zintl and H. Wattenberg, *Ber.*, 1922, **55**, [*B*], 3366; *A.*, ii, 871.

[59] I. M. Kolthoff, *Z. anal. Chem.*, 1922, **61**, 433; *A.*, ii, 864.

[60] N. Kanô, *J. Chem. Soc. Japan*, 1922, **43**, 556; *A.*, ii, 719.

[61] E. R. Bishop, E. B. Kettridge, and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1922, **44**, 135; *A.*, ii, 308.

[62] D. O. Jones and H. R. Lee, *J. Ind. Eng. Chem.*, 1922, **14**, 46; *A.*, ii, 239.

PHYSIOLOGICAL CHEMISTRY.

THE sad death of Benjamin Moore early in this year deprived Bio-
chemistry of a brilliant and daring thinker.   A pupil of Sir Edward
Sharpey Schafer, he later was the first occupant of the chair of Bio-
chemistry at Liverpool.   While there, he and Mr. E. Whitley founded
the *Biochemical Journal*, which, originally a private venture, later
became the official publication of the Biochemical Society.   A period
of research on behalf of the Medical Research Council followed his
resignation from Liverpool, but in 1920 he returned to academic
life as first Professor of Biochemistry at Oxford.   Unfortunately,
his tenure of this post was for little more than a year.   His loss as
a teacher and an investigator is a severe one.   The ranks of British
men of science have been further depleted by the deaths of Dr. A. D.
Waller, Professor of Physiology at London University, and·the
Hon. H. V. Onslow.   Few who have read the valuable papers on
biochemistry or genetics published from Onslow's Cambridge
laboratory can have been aware that the whole of these careful
researches were directed from an invalid's couch as the result of an
accident in undergraduate days which paralysed him from the waist.
    Amongst our foreign colleagues, we note with regret the loss of
W. Palladin, the eminent Russian plant physiologist and biochemist,
a pupil of Timiriazeff and latterly Professor at Petrograd ;   of
Takamine, best known for his isolation of adrenalin ;   of C. A.
Pekelharing, Emeritus Professor of Physiological Chemistry at
Utrecht ;   and of Franz Hofmeister, the eminent investigator who for
many years was Professor of Physiological Chemistry at Strassbourg.
    Whilst the multiplication of new journals is generally to be de-
plored, we may perhaps except the *Journal of Biochemistry*, edited
by Prof. Kakiuchi of Tokyo Imperial University, since it is obvious
that the wide interest in biochemistry apparent in Japan should be
served by a medium for home publication.   The contents are pub-
lished in English, German, and French.   On the other hand, the
appearance of the *Journal of Metabolic Research*, edited by F. M.
Allen in the U.S.A., is, to our mind, less excusable.   From a perusal
of the papers in the numbers which have appeared there seems no
adequate reason why existing periodicals should not have served
for their publication.   One fears that America is following the bad
example of Germany in this matter.
    Of the new books, attention must be directed to " Proteins and
the Theory of Colloidal Behaviour," by Jaques Loeb, which deals
in a remarkably clear manner with many problems of great import-

ance to biochemists. The great interest shown on all sides in the so-called vitamins is illustrated by the recent appearance of a large number of volumes dealing with these substances. Apart from the many more or less popularly-written books, amongst which special reference should be made to " Vitamins and the Choice òf Food," by V. G. Plimmer and R. H. A. Plimmer, several valuable reviews with extensive bibliographies have been published. " The Vitamins," compiled by C. Sherman and S. L. Smith, and published by the American Chemical Society, is especially good, whilst a second edition of " Die Vitamine," by C. Funk, and an English translation of it by Dubin, are also welcome. Many new editions have also appeared; " Oxidations and Reductions in the Animal Body," by H. D. Dakin (2nd ed.); " The Determination of Hydrogen Ions," by W. M. Clark (2nd ed.); " Die Wasserstoffionenkonzentration, ihre Bedeutung für die Biologie und die Methoden ihrer Messung," by L. Michaelis, Part I (2nd ed., to be issued in three parts); " Les Colloides," by J. Duclaux (2nd ed.); and " Physikalische Chemie der Zelle und Gewebe," by R. Hober (5th ed., Part I). A valuable monograph on " Hexosamines, their Derivatives and Mucins and Mucoids," based on the author's researches, has been published from the Rockefeller Institute for Medical Research by P. A. Levene. The unwieldy "Handbuch der biologischen Arbeitsmethoden," edited by E. Abderhalden, continues to appear, but the later numbers are not such as will dispel the feeling of disappointment and irritation expressed by Professor Barger in his last year's Report. Two biographical studies have been published which are of interest to biochemists. " Pasteur and his Life," by Descour, is delightful and will share distinction with Vallery Radot's well-known book. On the other hand, a sense of disappointment may follo the perusal of the autobiography " Aus meinem Leben " of Emil Fischer, especially if one compares it with the very good biography by J. Kurt Hoesch which appeared in the pages of the *Berichte*. In connexion with the Pasteur Centenary, Masson et Cie are issuing an edition of the classical works of this master. The first two volumes, " Disymétrie moléculaire " and " Fermentations et générations dites spontanées," are about to appear.

Amino-acids and Proteins.*

No outstanding discovery marks this year's work in the field of protein chemistry, but steady progress can be reported. The diffi-

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* Professor Barger has asked me to mention that in referring to the work of R. Willstätter and E. Waldschmidt Leitz (*Ber.*, 1921, **54**, [*B*], 2988) in this section of his last year's Report he inadvertently omitted to state that F. W. Foreman had described a similar method previously (*Biochem. J.*, 1920, **14**, 451).

culties of separating the products of hydrolysis of proteins make welcome the method described by H. W. Buston and S. B. Schryver,[1] which enables clean mixtures of amino-acids to be separated with ease from protein hydrolysates or other sources in a form convenient for further fractionation. A protein hydrolysate, after removal of tyrosine and the diamino-acids by the usual methods, is treated with baryta and alcohol, and carbon dioxide is passed. Several fractions of the barium salts of the carbamates of the amino-acids, having the general formula $RCH{<}^{NH_3CO_3}_{-CO_2}{>}Ba$, ascribed by Siegfried,[2] may be obtained.

The barium precipitates on decomposition yield clean, semi-crystalline mixtures of amino-acids. It is claimed that the method will effect the quantitative removal of amino-nitrogen from a solution.

Another preliminary fractionation of the amino-acids which may eventually be of considerable value is described by G. L. Foster and C. L. A. Smith,[3] who apply on a laboratory scale the method of K. Ikeda and S. Susuki [4] in which a direct current is passed through a solution of the amino-acids, placed in a three-compartment cell. The units which are predominantly acid, such as glutamic acid, migrate to the anode, the basic substances, lysine, arginine, etc., travel to the cathode, and the more or less neutral units remain in the central compartment. The method appears to yield relatively large amounts of clean preparations of arginine and lysine.

R. Engeland [5] has described a method in which the monoamino-acids are converted into the corresponding betaines as a means of estimating certain units. From elastin he has isolated the betaine of what he believes to be a hitherto unknown amino-acid with the formula $C_{13}H_{26}O_4N_2$.

The general feeling that our knowledge of the sulphur-containing constituents of the proteins is lamentably deficient is reflected in several papers. Of particular interest is the announcement by J. H. Mueller [6] of his isolation of a new amino-acid containing sulphur from the products of hydrolysis of commercial caseinogen with sulphuric acid. Further details of this acid will be awaited with great interest, but the preliminary communication states that there are indications that it is a straight-chain compound with two amino-groups and probably two carboxyl groups. It is uncertain in what form the sulphur is present. W. F. Hoffmann and R. A. Gortner [7]

[1] *Biochem. J.*, 1921, **15**, 636; *A.*, 1921, i, 182.
[2] *Z. physiol. Chem.*, 1905, **46**, 401; *A.*, 1906, i, 324.
[3] *Proc. Soc. Exp. Biol. Med.*, 1922, **19**, 348.
[4] *U.S. Pat.* 1015891, 1912.
[5] *Z. physiol. Chem.*, 1922, **120**, 130; *A.*, ii, 536.
[6] *Proc. Soc. Exp. Biol. Med.*, 1922, **19**, 161.
[7] *J. Amer. Chem. Soc.*, 1922, **44**, 341; *A.*, i, 429.

have studied the effect of acid hydrolysis on cystine and report interesting observations. Pure cystine, boiled for varying lengths of time with 20 per cent. hydrochloric acid, underwent only slow decomposition, and the authors do not think there is appreciable decomposition of cystine during the usual protein hydrolysis. The small amount of sulphur liberated was either in the form of hydrogen sulphide or of free sulphur. The cystine after hydrolysis showed certain differences from the original product in being less readily precipitated by phosphotungstic acid, optically inactive, more soluble in water, and crystallising in prisms. The derivatives of the two forms of cystine showed dissimilarities. The authors advance the suggestion that the isomeric cystine they have isolated is identical with the synthetic product of Erlenmeyer and Stoop [8] and of Fischer and Raske,[9] and that " plate " cystine as obtained from the hydrolysis of proteins has never been synthesised.

The unsatisfactory nature of the existing methods for the analysis of the diamino-acid fraction of protein hydrolysates is apparent to all who have had occasion to use them. Recently J. L. Rosedale,[10] in an investigation of the diamino-acid content of muscle proteins, has referred to the inconsistencies of the results obtained by the well-known method of Van Slyke.

The inaccuracies associated with the estimation of the acids in this fraction are largely bound up with those due to the method of determining arginine, as pointed out by R. H. A. Plimmer,[11] who also modified the process to render it somewhat more trustworthy. Even when there is reason to believe that the estimation of arginine is satisfactory, the value for histidine, and therefore indirectly that for lysine, is based on the assumption that the whole of the non-amino-nitrogen of the fraction is represented by histidine and arginine. That this assumption is liable to lead to serious error is now definitely proven by the investigations of D. D. Van Slyke and A. Hiller.[12] They found that the values for histidine obtained by the usual method and those based on K. K. Koessler and M. T. Hanke's [13] colorimetric process show agreement in the case of caseinogen, edestin, and fibrin, but a considerable difference with gelatin. This led them to fractionate the phosphotungstic acid precipitate obtained from hydrolysed gelatin, as a result of which evidence was obtained of the presence of an unidentified base. Attempts to obtain the free base in a crystalline condition

[8] *Ber.*, 1908, **41**, 893; *A.*, 1908, i, 325.
[9] *Annalen,* 1904, **337**, 222; *A.*, 1905, i, 119.
[10] *Biochem. J.*, 1922, **16**, 27; *A.*, i, 492.
[11] *Ibid.*, 1916, **10**, 115; *A.*, 1916, ii, 460.
[12] *Proc. Nat. Acad. Sci.*, 1921, **7**, 185; *A.*, i, 63.
[13] *J. Biol. Chem.*, 1919, **39**, 497; *A.*, 1920, ii, 67.

were unsuccessful.   It is hygroscopic, decomposes slowly at 100°, and has a ratio of nitrogen to amino-nitrogen of 2 : 1.   As the value remains constant after treatment with acids, it is concluded that the substance is not a peptide.   Further information of .this new basic constituent of the proteins will be awaited with great interest.

The presence of hydroxyaspartic acid among the products of hydrolysis of proteins once reported by Z. H. Skraup [14] has not been confirmed by a careful examination of the products of tryptic digestion of caseinogen by H. D. Dakin.[15]   Further study of this acid has, however, been facilitated by his synthesis of the para- and anti-hydroxyaspartic acids from chloromalic acid and ammonia.   Separation of the isomerides was effected by fractional crystallisation, whilst in a later paper [16] is described the resolution of the anti-acid by means of the strychnine and quinine salts.   The para-acid was not resolved.

Gradually, but very slowly, information on the difficult problem of the mode of linking of the amino-acids in proteins is being collected, but it is somewhat surprising that a comparatively simple class such as the protamines has not been the subject of more extensive study from this point of view.   R. E. Gross [17] has, however, isolated from the products of hydrolysis of clupeine a dipeptide-like substance consisting of at least two arginine molecules.   He has also confirmed Nelson Gerhardt's [18] deduction that in salmine and clupeine the monoamino-acids are linked together. Clupeine has also been investigated by H. Steudel and E. Peiser,[19] who have prepared combinations of the protamine with guanylic acid and yeast-nucleic acid in an attempt to elucidate the constitution of the nucleo-proteins.   E. Abderhalden [20] has succeeded in isolating at intermediate stages in the hydrolysis of silk fibroin considerable quantities of a d-alanyl-glycine anhydride and small quantities of glycyl-l-tyrosine anhydride, and of a compound containing serine, d-alanine, and glycine.   Incidentally his examination of this protein accounted for 86·4 per cent. of the total amino-acids as compared with previous figures in the neighbourhood of 70 per cent.   The current idea that the free amino-nitrogen of proteins is related to the lysine content receives support from the

[14] *Ber.*, 1904, **37**, 1596; *A.*, 1904, i, 538.
[15] *J. Biol. Chem.*, 1921, **48**, 273; *A.*, i, 143.
[16] *Ibid.*, 1922, **50**, 403; *A.*, i, 430.
[17] *Z. physiol. Chem.*, 1922, **120**, 167; *A.*, i, 784.
[18] *Ibid.*, 1919, **105**, 165; *A.*, 1919, i, 503.
[19] *Ibid.*, 1922, **120**, 207; *A.*, i, 784.
[20] *Ibid.*, 1922, **122**, 298; *A.*, i, 1200.

work of M. S. Dunn and H. B. Lewis,[21] who have studied the distribution of nitrogen in caseinogen and deaminised caseinogen. Lysine was found to be absent from the products of the hydrolysis of the deaminated protein and some destruction of tyrosine had also occurred. In a later paper,[22] they record that the deaminated caseinogen can be hydrolysed by pepsin and trypsin, but at a slower rate than in the case of the untreated protein, whilst experiments on a dog indicate that, when tolerated, it can also be metabolised by the organism.

Protein Metabolism.

At least one outstanding paper on protein metabolism has appeared during the twelve months under review. This is the paper by C. J. Martin and R. Robison[23] on the minimum nitrogen expenditure of man and the biological value of various proteins for human nutrition. Its appearance marks a very important advance in this branch of the science of nutrition. The realisation that the proteins do not have a uniform value in nutrition was gaining ground at the close of the last century, and was, indeed, definitely formulated by Rubner in 1897, but the term " biological value " which is to-day so widely employed in this connexion was introduced by Karl Thomas[24] in 1909. This investigator defined the " biological value " of a protein as the number of parts of body nitrogen replaceable by 100 parts of the nitrogen of the foodstuff, and the values he determined have been extensively employed by physiologists. Martin and Robison began their investigation with the modest object of redetermining the relative values for certain cereal proteins, but they soon found great difficulty in arriving at values which could justifiably be compared and began to suspect that a number of the earlier investigations were open to criticism. Accordingly, they began a careful investigation of the conditions under which valid results might be obtained, and their paper represents not only a sound criticism of earlier determinations, but also a most valuable study of the experimental methods concerned. They point out that Thomas adopted an experimental method based on the assumption that the value of any protein for biological purposes remains uniform whatever the amount taken. The misleading nature of this procedure can best be appreciated if the case of gelatin is considered. The various possibilities are explained by the authors by means of the diagram reproduced on p. 188, in which the abscissæ represent real nitrogen intake and the

[21] *J. Biol. Chem.*, 1921, **49**, 327; *A.*, i, 279.

[22] *Ibid.*, 343; *A.*, i, 292.

[23] *Biochem. J.*, 1922, **16**, 407.

[24] *Arch. Physiol.*, 1909, 219.

ordinates real nitrogen output. If $OM = m$ represent the output
of nitrogen on a nitrogen-free diet of adequate fuel value, then m is
equal to the nitrogen minimum.

The administration of an ideal protein (biological value 100,
and utilised without waste) in gradually increasing amounts will
result in no change in the amount of excreted nitrogen, m, until the
intake equals that value, at which point, E, where $ME = MO$,
the body will be in nitrogen equilibrium. When the intake rises
above m, the graph of intake and output will follow the line EE_n
at an angle of 45° to the axis (unless the body is growing or has pre-
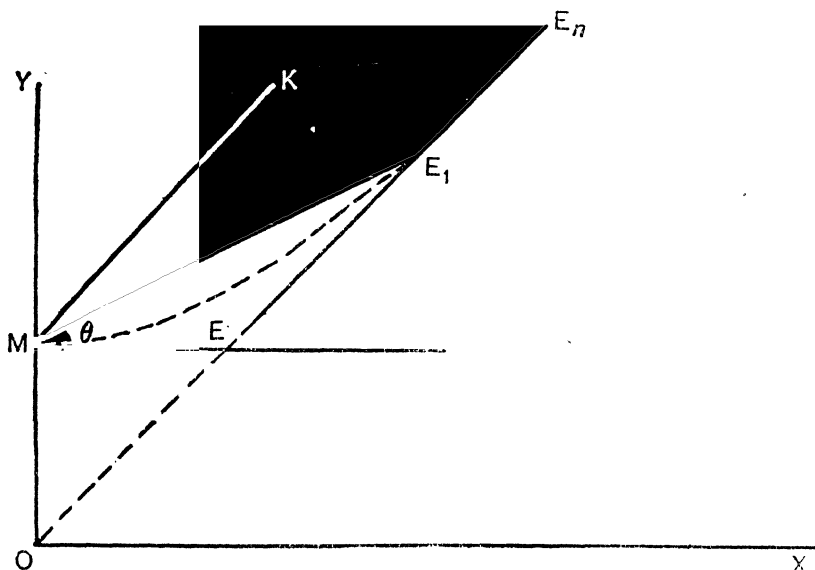
FIG. 1.

viously been starved of nitrogen). Ordinary proteins with biological
values less than 100 will not suffice for equilibrium to be established
at the point E, but at some other point E_1. Before nitrogen
equilibrium is reached, the graph will follow the line ME_1, which
may be either straight or curved, depending on the indivisibility
of the nitrogen requirements of the body and the uniform economy
with varying nitrogen intake. If these conditions are obtained,
then Thomas's formula,

$$BV = 100 \frac{\text{Urine N on N-free diet} + \text{faeces N} + \text{balance}}{\text{N intake}},$$

becomes $BV = 100 (1 - \tan \theta)$.

In the case of a protein inadequate to supply any portion of the
requirements of the organism, the graph will be the line MK parallel

to OE_m; that is, the nitrogen output will always equal the nitrogen intake plus the value m. That is, $BV = 100\ (1 - \tan 45°) = 0$.

Whilst there was very little reason for assuming that these graphs would prove to be straight lines, the experimental determination of a number of points at different levels of intake of the same protein demonstrated that in the case of bread approximation to a straight line actually occurs. There was evidence that this may be also true for milk proteins. In the case of gelatin, however, the ratio certainly does not remain constant, and there is no indication that the amount of body nitrogen saved increases beyond that effected by the smallest amount of gelatin administered. It can therefore be seen that the application of Thomas's method is justifiable in the case of bread, doubtful with milk, and of no value in the case of gelatin. In cases where his method is not known to be trustworthy, the ratio body-N saved/food-N absorbed should be determined close to, but below, the point of equilibrium. In any case, the biological values derived from experiments of comparatively short duration have a limited significance. The value of gelatin in relation to the nitrogen requirements of man is also very fully treated in an interesting paper by R. Robison [25]; these researches have in addition served to provide further information regarding the distribution of nitrogen in the urine on diets low in nitrogen.[26]

Glutathione and Tissue Oxidations.

Reference was made in last year's Report to the discovery by Hopkins of an auto-oxidisable constituent of the cell, and further information regarding this remarkable substance has since been eagerly awaited. Late in the year our expectations were fulfilled by the appearance of a publication by F. G. Hopkins and M. Dixon.[27] This paper is concerned with significance of glutathione in the oxidative mechanisms of the cell, but chemists will welcome the statement that a full study of the chemical properties of this substance is in progress. It should not be a task of excessive difficulty to establish the mode of linking between the constituent aminoacids, cystine and glutamic acid, as a first step towards synthesis. The most striking fact reported in the new paper from the Cambridge laboratory is the apparent association, in oxidative and reductive processes, of the dipeptide with a tissue agency which is insoluble in water and resistant to a temperature of 100°, or to treatment with alcohol. It will be recalled that O. Meyerhof,[28] in 1918, demonstrated

[25] *Biochem. J.*, 1922, **16**, 111; *A.*, i, 488.

[26] *Ibid.*, 131; *A.*, i, 495.

[27] *J. Biol. Chem.*, 1922, **54**, 527.

[28] *Arch. Ges. Physiol.*, 1918, **170**, 428.

that the ability of a yeast extract or " Kochsaft " to give the nitro-prusside reaction showed a certain parallel with its power to restore the " respiration " of washed acetone yeast. His investigations showed that cystine had not the latter effect, but when thioglycollic acid or thiolactic acid was added to the washed yeast in a neutral or slightly acid medium, oxygen was absorbed in an amount larger than that required to oxidise the added acid to the disulphide form. Furthermore, Meyerhof demonstrated the even more remarkable fact that a similar action follows the addition of thioglycollic acid to a washed yeast which has been heated at 100°.

The parallel between Meyerhof's results and those now recorded by Hopkins and Dixon is at first sight a close one, but more detailed examination of the experimental data indicates that further inform-ation is necessary before a definite opinion on this point can be formed. The experiments at the Cambridge laboratory once again demonstrate how valuable may be the information obtained by the study of tissue activities before and after they have been thoroughly extracted to remove water-soluble components. By this means assistance in recognising the co-ferment of alcoholic ferment-ation was obtained by Harden and Young, whilst more recently both Meyerhof and Batelli and Stern have used this method with considerable success in their attempts to elucidate the nature of the oxidative mechanisms in the living cell. In Hopkins and Dixon's experiments it was found that fresh muscle-tissue, after being thoroughly washed, does not reduce methylene-blue, or reduces it very slowly, nor will such tissue show the absorption of oxygen and liberation of carbon dioxide which are characteristic of respir-ation. The addition of glutathione, which is, of course, one of the soluble constituents removed by the washing, to the washed tissue, suspended in a " buffered " phosphate solution, will not only restore the power to reduce methylene-blue, but also will enable the tissue to " respire." The most interesting point is, however, that the power to reduce the dye and to show respiration on addition of glutathione is displayed, not only by the washed tissue, but also by tissue which has been extracted thoroughly with boiling water or alcohol or which has been heated at 100°.

That the thermostable agent in the tissue residues shows a definite reducing power is demonstrated by the prompt reduction of the added oxidised form of glutathione, enabling the system to show reduction of methylene-blue or " respiration." The tissue residues must therefore contain a stable hydrogen donator, which is relatively insoluble in water, and presumably some form of stable primary catalytic system for which glutathione is a co-agent. The thermo-stable tissue factor activated by glutathione is sensitive to oxidation,

presumably owing to the slow oxidation of the relatively labile hydrogen atoms which in the normal system are so readily yielded to other acceptors. Even the transport of the labile hydrogen to atmospheric oxygen is accelerated by glutathione, and in this case the absorption of oxygen may be as much as 400 c.c. of oxygen per gram of dried material. This amount appears to be, from the approximate data available, about one-tenth of the total possible uptake of the original untreated tissue. The respiratory exchange of this process is about unity in the early stages, but falls off after a time to nearly zero. Hopkins and Dixon's paper contains a careful discussion of glutathione in relation to other systems of oxidative mechanism which are believed to exist. The molecule of glutathione is not oxidised anaërobically by washed tissues in the presence of methylene-blue as T. Thunberg [29] found was the case with such substances as succinic acid and glutamic acid. Moreover, it does not suffer oxidation by atmospheric oxygen as a result of surface action such as occurred in the case of certain amino-acids in the presence of charcoal studied by Warburg.[30] Apparently the molecule of the dipeptide is stable, apart from the reversible change of the sulphur groupings which is its main characteristic. So far as the authors can ascertain, glutathione takes no part in such oxidising agencies as are associated with the " oxydases " present in the cold-water extracts of tissues. The nature of the oxidation-reduction systems existing in washed tissues still requires a good deal of elucidation, but it is quite clear that the thermolabile and unstable factors which are probably responsible for the effects observed by Thunberg (the " oxydones " of Batelli and Stern [31]) are distinct from the thermostable factors described by Hopkins and Dixon and by Meyerhof. It is rather in relation to the " respiratory substance " (Atmungskörper) and the oxidising system described by the latter investigator that glutathione must be considered, and H. D. Dakin,[32] for one, has suggested that Meyerhof's activator to respiratory activity in killed washed yeast may be none other than the new dipeptide.

The experiments of Meyerhof on the power of thioglycollic acid to restore the " respiration " of killed, washed yeast are of great interest in the light of Hopkins and Dixon's observations that washed tissues actually have the power to effect the reduction of dithiodiglycollic acid :

$$S_2(CH_2 \cdot CO_2H)_2 \rightarrow 2SH \cdot CH_2 \cdot CO_2H.$$
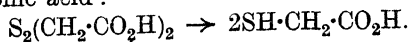
[29] *Skand. Arch. Physiol.*, 1920, **40**, 1; *A.*, 1920, i, 784.

[30] *Biochem. Z.*, 1921, **113**, 257; *A.*, 1921, i, 230.

[31] " Ueber den Mechanismus der Oxydationsvorgänge im Tierorganismus," Jena, 1914.

[32] *Physiol. Rev.*, 1922, **1**, 394.

Dithiodiglycollic acid promotes oxygen transport less effectively than does oxidised glutathione in the change.

$$
\begin{array}{ccccc}
\text{CH}_2\text{—S—S—CH}_2 & & & \text{CH}_2\text{—SH} \\
\text{CH·NH···} & \text{CH·NH···} & \longrightarrow & \text{CH·NH···} \\
\text{CO···} \quad \text{G} & \text{CO···} \quad \text{G} & & \text{CO···} \quad \text{G}
\end{array}
$$
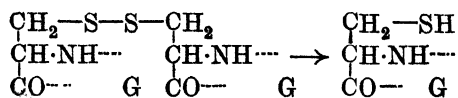
If the conception of the " Atmungskörper " be such that it is regarded as representing the action of two or more substances each related to some particular aspect of respiratory oxidation, then glutathione is one of these, its activity being mainly relative to respiratory factors which are thermostable.   We may perhaps quote an extract from the paper by Hopkins and Dixon : " The facts suggest that coexisting in living tissues with the special enzymic mechanism is a thermostable mechanism for oxidations and reductions.   Materials in close association with structural elements are oxidised, aërobically or anaërobically, with the coagency of the sulphur groups of glutathione."   The nature of the thermostable agent or agents residual in the washed tissues is as yet undiscovered.

Mammary Secretion.

A study of the origin of milk fat and its relation to the metabolism of phosphorus has been made by J. Sheehy,[33] who finds that carbohydrate and fat can replace each other in the diet for the manufacture of fat by the mammary gland.   His conclusion that the immediate precursor is a diffusible substance of the nature of a phosphatide constitutes further support for the work of E. B. Meigs, N. R. Blatherwick, and C. A. Carey,[34, 35] who showed that the increase in inorganic phosphate after the blood has passed through the mammary gland is sufficient to account for the whole of the milk fat having been formed from a precursor of that type.   The significance of phosphorus in the transport of fat in the animal body is also emphasised by Bloor in a useful review of the subject.[36]

The significance of colostrum remains obscure.   J. H. Lewis and H. G. Wells [37] regard it as a source from which the young derive the specific anti-bodies of the maternal organism which are believed to be associated with the globulin fraction.   Support for this view may perhaps be derived from the experiments of T. Smith and R. B. Little,[38] who found that calves are more liable to succumb to

[33] *Biochem. J.*, 1921, **15**, 703.

[34] *J. Biol. Chem.*, 1919, **37**, 1; *A.*, 1020, i, 203.

[35] *Ibid.*, 1920, **40**, 469.

[36] *Physiol. Rev.*, 1922, **2**, 92.

[37] *J. Amer. Med. Assoc.*, 1922, **78**, 863.

[38] *J. Exper. Med.*, 1922, **36**, 181.

bacterial invasion when they are deprived of colostrum. Whether this protective action is directly due to anti-bodies or indirectly to a strengthening of the resistant powers of the organism by other factors is not yet clear, but it must be recalled that colostrum is richer than ordinary milk in vitamin-A, and that there is a good deal of evidence that this substance assists to maintain the defence of the body's tissues.[39] It would now seem to be established with some certainty that the diet of the lactating female is the chief factor determining the concentration of vitamins in the milk, but the paper by C. Kennedy and R. A. Dutcher [40] is important because it proves that the vitamin value of the milk of cows can be maintained throughout the winter period of stall feeding by care in the selection of a ration consisting of a proper balance between grains and leafy foods. The far-reaching influence of the diet of the mother on the nutritive value of the milk is further illustrated by the experiments of G. Hartwell. In a study of the effect of diet on mammary secretion,[41] she investigated the effect of changing the balance of the chief food components, and discovered that an excess of protein tends to cause an interference with the normal lactation leading to nutritional disturbances in the young. Further experiments [42, 43] confirmed this observation, but the cause of this effect of the protein has not yet been ascertained with certainty. Apparently the high protein diet is not in itself deleterious, a view supported by the results of J. C. Drummond, G. P. Crowden, and E. L. G. Hill,[44] but it seems to demand a readjustment in the balance of certain other food units. The beneficial influence of a supplement of fresh milk or marmite (commercial yeast extract) led to suggestions being advanced that the vitamin-B may be the factor concerned,[44, 45] and further researches by Hartwell appear to confirm this view.[46] In continuance of her studies on the influence of proteins on mammary secretion, Miss Hartwell has been unable to obtain evidence that edestin possesses any specific action as a galactogogue.[47]

Sugar Metabolism and Diabetes.

The mechanism by which dextrose is broken down in the animal body is a subject which continues to attract widespread interest.

[39] Drummond, Coward, and Watson, *Biochem. J.*, 1921, **15**, 540.
[40] *J. Biol. Chem.*, 1922, **50**, 339.
[41] *Biochem. J.*, 1921, **15**, 141.
[42] *Ibid.*, 563.
[43] *Ibid.*, 1922, **16**, 78.
[44] *J. Physiol.*, 1922, **56**, 413.
[45] C. Kennedy and L. S. Palmer, *J. Biol. Chem.*, 1922, **54**, 217.
[46] *Biochem. J.*, 1922, **16**, 825.
[47] *Lancet*, 1921, i, 323.

There is a tendency at the moment, however, for chief attention to be transferred from the intermediate stages, in which the hexose molecule is degraded, to the elucidation of the changes which are believed to occur before the sugar molecule is actually broken.

The researches of Embden and his co-workers [48] have made it appear probable that phosphorus compounds are concerned in the early stages of the metabolism of hexoses, and his conception of the rôle of hexosephosphoric acid in the molecule of the "lactacidogen" complex presents an interesting parallel with the current views on the significance of this acid in the fermentation of sugars by yeast. D. L. Foster and D. M. Moyle [49] have recently found that chopped muscle not only has the power to break down added hexosephosphate *in vitro*, but also has the ability to synthesise that complex from dextrose and phosphoric acid.   On all hands, evidence is accumulating that the hexose molecule, before it can be broken down in the normal manner by living cells, must pass through the state of hexosephosphate, and there can be little doubt that during this process a rearrangement of the molecule occurs with the production of a highly reactive form of the sugar.

The rôle of phosphates in the oxidation of hexoses in the living cell has led A. Harden and F. R. Henley [50] to examine the significance of these salts in the oxidation of dextrose by hydrogen peroxide. W. Löb and his co-workers [51] believe that the oxidation depends on the hydroxyl-ion concentration and that phosphates exert a specific accelerating effect on the reaction.   This view was supported by Witzemann,[52] who further suggested that the specific action of the phosphates might be attributable to the necessity of the intermediate formation of a hexosephosphate.   Harden and Henley's investigations show, however, that the action of phosphates in this oxidation is not specific, but that it depends on their power to regulate the reaction of the medium.   Other " buffer " systems were equally effective.   H. Elias and St. Weiss [53] have found that intravenous injections of sodium mono- and di-phosphates may lower both alimentary and diabetic hyperglycæmia, but they do not influence the level of blood-sugar in normal subjects.   It is suggested that in the former cases either the combustion of dextrose is stimulated or that storage of hexose, possibly as a phosphoric acid complex, may occur.

[48] *Z. physiol. Chem.*, 1914, **93**, 1, 94, 124; *A.*, 1915, i, 344, 345, 346.
[49] *Biochem. J.*, 1921, **15**, 672; *A.*, i, 398.
[50] *Ibid.*, 1922, **16**, 143; *A.*, i, 433.
[51] *Biochem. Z.*, 1911, **32**, 43; 1912, **46**, 288; 1915, **68**, 368; *A.*, 1911, ii, 504; 1913, i, 125; 1915, ii, 247.
[52] *J. Biol. Chem.*, 1920, **45**, 1; *A.*, 1921, i, 160.
[53] *Weiner. Arch. inn. Med.*, 1922, **4**, 29; *A.*, i, 1085.

Speculation as to the reactive form of sugar produced by the hypothetical preliminary rearrangement is already active. A. Bornstein and K. Holm [54] believe it to be lævulose or a related substance, but probably more support is to be given to the suggestion that it is the reactive ethylene-oxide form of dextrose. J. A. Hewitt and J. Pryde [55] have already presented evidence that solutions of dextrose and lævulose in contact with the mucous membrane of the intestine are converted into γ-glucose. Such views have led to a re-examination of the nature of the reducing substances of the blood by E. A. Cooper and H. Walker.[56] They have found that dextrose is the chief reducing substance present, but that other reducing substances of a more complex nature are occasionally detectable. They obtained no evidence, however, that human blood can transform dextrose or lævulose into the highly reactive ethylene-oxide forms, an observation which confirms the results of J. A. Hewitt and D. H. de Souza.[57]

More recently still, L. B. Winter and W. Smith [58] have definitely advanced the opinion that the sugar present in normal blood is an unstable form of glucose of low initial rotatory power and possibly the so-called γ-glucose or ethylene oxide form of dextrose. This view is based on their observations that in the protein-free filtrates of normal blood the copper-reducing values and those obtained by polarimetric determinations at first show disagreement, but after some time, two to three days, the values in the latter case gradually approach the former until agreement is reached. In the case of diabetic bloods, however, the polarimetric readings gave higher values than the copper method; but here again, after a period of time, agreement between the two determinations was obtained.

It is suggested that the blood-sugar in cases of diabetes is the α- β-dextrose and that the failure of the organism to utilise sugar in this disease is due to the absence or inactivity of an enzyme which in the normal subject converts the α- and β-sugars into the active γ-form. Their suggestions are of very great interest and may lead to results of the highest importance, but the evidence on which they are advanced is far from being as convincing as might be desired.

The inability of the diabetic organism to utilise dextrose has for a long time been associated with a disturbance of the internal secretion of the pancreas. The classical researches of von Mering

[54] *Biochem. Z.*, 1922, **130**, 209; *A.*, i, 890.
[55] *Biochem. J.*, 1920, **14**, 395; *A.*, 1920, i, 508.
[56] *Ibid.*, 1921, **15**, 415; *A.*, i, 698.
[57] *Ibid.*, 667; *A.*, i, 395.
[58] *J. Physiol.*, 1922, **57**, 100.

and Minkowski [59] demonstrated that a condition closely resembling human diabetes mellitus may be established in dogs by complete extirpation of the pancreas.

This led Lepine [60] to suggest that the condition is due to the withdrawal of an internal secretion of the pancreas which is essential for the utilisation of sugar. Many attempts have since been made to demonstrate the existence of a pancreatic hormaone, chiefly by the administration of extracts prepared by various means from the gland,[61, 62, 63, 64, 65] but although occasionally evidence was obtained of an improved utilisation or of a temporary reduction of the sugar output, the results were never conclusive. The cause of the uncertain activity of the preparations was not definitely ascertained, but by some it was considered to be the destructive action of trypsin. These views, together with pathological evidence that the islets of Langerhans frequently show atrophy in cases of diabetes, have led two young Canadian clinicians, F. G. Banting and C. H. Best, of Toronto, to investigate the action of extracts of the islets alone in the treatment of experimental diabetes in dogs. This was attained by preparing extracts either from fœtal glands, in which only the islet tissue was present, or from glands in which atrophy of the other parts of the structure had been induced by ligature of the pancreatic duct. The administration of these extracts to diabetic dogs was found to bring about a very marked fall in the blood- and urinary- sugar and to improve the general condition of the animals in a most striking manner.[66] Encouraged by their success, they proceeded to attempt the extraction of the active substance from normal ox pancreas, using alcohol as a means of preventing enzyme action, a method previously employed by Scott.[62] The material thus prepared proved so potent in the treatment of dogs that it was tried in a severe case of diabetes in a boy of fourteen. The result was a reduction of the blood-sugar by 25 per cent.[67]

To the active substance present in these extracts the discoverers give the name " insulin." By mobilising a team of research workers, the Toronto investigators have in a remarkably short time reported a considerable progress in the study of this new substance. The

[59] *Arch. exp. Path. Pharm.*, 1889, **31**, 371.
[60] " Le diabète sucre," Paris, 1909.
[61] Starling and Knowlton, *J. Physiol.*, 1912, **45**, 146.
[62] E. L. Scott, *Amer. J. Physiol.*, 1912, **29**, 3.
[63] J. R. Murlin and B. Kramer, *J. Biol. Chem.*, 1913, **15**, 365,
[64] Kleiner, *ibid.*, 1919, **40**, 153.
[65] Clarke, *Johns Hopkins Hosp. Rep.*, **18**, 229.
[66] *J. Lab. Clin. Med.*, 1922, **7**, 251.
[67] *Ibid.*, 260.

method of preparation has been improved by J. B. Collip,[68] whose process, now generally employed, is a prolonged and rather laborious fractionation by means of alcohol.

The administration of insulin not only reduces the hyperglycæmia in diabetes, but also that associated with sugar puncture, adrenalin, or ether anæsthesia,[69] which may help to explain the observations of L. Adler [70] that the simultaneous administration of pancreatic extract, made from hibernating hedgehogs, more or less completely suppresses the action of adrenalin and other substances which, given alone, rouse the hibernating animal and restore its body temperature to summer level. Furthermore, insulin will induce a condition of hypoglycæmia in normal animals. This fact is made the basis of the provisional pharmacological standardisation of insulin extracts. A unit dose is described as that amount which on subcutaneous injection will reduce the percentage of blood-sugar in a rabbit of 2 kg., which has been starved for sixteen to twenty-four hours, to 0·045 per cent.[71] The latter figure is chosen because the fall of the blood-sugar to that level is marked in rabbits by the appearance of characteristic symptoms which take the form of violent convulsions and which, with intervals of coma, terminate fatally. The extraordinary fact appears established that there is a definite relationship between the amount of insulin and that of sugar catabolised, for the symptoms of an overdose of insulin can immediately be dispelled by the administration of an appropriate dose of sugar. This also applies to the treatment of human cases.

In addition, to restoring a normal blood-sugar level in diabetics, insulin tends to restore the respiratory quotient to normal figure, and also to cause the disappearance of the so-called " acetone bodies " from the urine. In experimental animals, it has also been found to re-establish the normal balance between glycogen and fat in the liver and to restore a normal glycogen content of the heart. The clinical use of insulin is described by Banting, Best, Collip, Campbell, and Fletcher,[72] who find that the administration of suitable doses by subcutaneous injection twice daily removes the cardinal symptoms in a few hours, and, enabling a higher calorific intake to be consumed, leads to an increase of weight and marked improvement in the mental and physical condition of the patient. Much work remains to be done before the remedy can be widely employed, and no small part of its future success will probably depend on whether during

[68] Banting, Best, Collip, Macleod, and Noble, *Trans. Roy. Soc. Canada*, 1922, **16**, Sec.

[69] Macleod, *Brit. Med. J.*, 1922, 833.

[70] *Arch. exp. Path. Pharm.*, 1921, **91**, 110; *A.*, i, 195.

[71] *Amer. J. Physiol.*, 1922, **42**, 162.

[72] *Canad. Med. Assoc. J.*, March, 1922.

the period of insulin treatment the pancreas is able gradually to restore its normal function. However this may be, full credit must be given to the Toronto investigators for a very thorough and painstaking piece of research which has yielded results of fundamental importance both in the clinical treatment of diabetes and in the purely scientific study of sugar consumption in the animal body. It is a regrettable fact that already the armchair critics are busy with attempts to belittle this fine work, and many of the letters which have appeared in the medical Press sadly remind one that the conservatism and jealousies which opposed such advances as were instituted by Pasteur and Lister are by no means dead.

Calcium Metabolism and Vitamins.

Although Professor Barger treated this subject in last year's Report, the advances which have been made during the last twelve months, as well as the widespread interest in this subject, lead me to devote attention to it again this year. Whatever may be their views on the ætiology of rickets, practically all authorities acknowledge the beneficial effects of treatment of this disorder with cod-liver oil. On the one hand, the supporters of theories associating rickets with unhygienic environment or bacterial infection attribute the influence of cod-liver oil to its indirect action in increasing the resistant powers of the body (Paton),[73] whilst those who favour the dietetic origin of the disease tend to ascribe its effect to the presence of an anti-rachitic vitamin. As Mellanby showed [74] in his experimental studies of rickets in dogs, the effect of fats in preventing rickets is roughly parallel to their power to promote growth, and accordingly he inclined to the view that the anti-rachitic vitamin is identical with vitamin-A.

The position has, however, been considerably obscured by a mass of published work on the subject which has appeared during the last year. It would be impossible in the space at my disposal to attempt a review of this work in its entirety, but from it three main conclusions may be drawn. The first is the observation, now generally confirmed, that sunlight or exposure to ultra-violet light will prevent or cure rickets in spite of the diet being defective; [75] secondly, it is apparent that not only a deficiency of some factor present in cod-liver and other oils may induce the onset of rickets, but also that this condition may result from a disturbance of the calcium–phosphate balance in the diet even when the hypothetical

[73] *Brit. Med. J.*, 1922, i, 379; *Glasgow Med. J.*, 1922, **97,** 129.
[74] Special Report No. 61, Medical Research Council, 1921.
[75] A. F. Hess and L. J. Unger, *J. Amer. Med. Assoc.*, 1921, **77,** 39; *Amer. J. Dis. Child.*, 1921, **22,** 186; *Proc. Soc. Exper. Biol. Med.*, 1921, **18,** 298.

anti-rachitic vitamin is present in what is believed to be a sufficient amount.[76] Finally, McCollum and his co-workers suspect the existence of an anti-rachitic vitamin distinct from the vitamin-A, which they regard as mainly concerned with growth.[77]

Confirmation of the beneficial action of ultra-violet light has been obtained by most workers, and a particularly interesting investigation which covers this point is reported in a communication by H. Chick, E. L. Dalyell, M. Hume, H. M. M. Nackay, H. H. Smith, and H. Wimberger,[78] who have for two years been making a close study of deficiency diseases in Austria. With regard to the suggestion of the existence of more than one vitamin in certain fats, one feels that the evidence submitted by McCollum tends to support such a view, but that he has perhaps not yet considered the matter sufficiently from the quantitative point of view. As S. S. Zilva and I. Muira [79] showed, cod-liver oil may contain a concentration of vitamin-A more than 200 times greater than that found in butter, and to our mind some of McCollum's results might be explained on this basis as well as by assuming the existence of two separate factors. This has been also pointed out by Zilva.[80] The apparent difference in the destruction of the two factors reported by E. V. McCollum, N. Simmonds, and J. E. Becker,[81] is, however, rather strong evidence in favour of two separate factors, one of which is concerned in growth and the prevention of keratomalacia and the other playing a rôle in calcium deposition.

The whole subject of rickets is reviewed in an excellent monograph by V. Korenchevsky,[82] which contains a very extensive bibliography. The conclusions he has drawn from this review and from his own careful experimental work give general support to the dietetic theories of the origin of the disease. For the prevention of rickets the following factors may, in his opinion, be taken as most important : adequate amounts in the mother's diet of anti-rachitic factor (? vitamin-A), calcium, and phosphates during pregnancy, and especially during lactation ; a similar diet for the infant, and abundant light, fresh air, and exercise. Similar conclusions are also drawn from another quarter by H. C. Mann, who has just published the results of a careful clinical investigation into the

[76] E. V. McCollum, N. Simmonds, P. G. Shipley, and E. A. Park, *J. Biol. Chem.*, 1921, **47**, 507; *A.*, 1921, i, 757.

[77] E. V. McCollum, N. Simmonds, J. E. Becker, and P. G. Shipley, *Bull. John Hopkins Hosp.*, 1922, **33**, 229; Shipley, Park, McCollum, and Simmonds, *Amer. J. Hyg.*, 1921, **1**, 512; *Amer. J. Dis. Child.*, 1922, **23**, 91.

[78] *Lancet*, 1922, ii, 7.

[79] *Ibid.*, 1921, i, 323.

[80] *Ibid.*, 1922, i, 1244.

[81] *J. Biol. Chem.*, 1922, **53**, 292.

[82] Special Report No. 71, Medical Research Council, 1922.

relative importance of environment and diet as factors in the causation of rickets in London children.[83] In view of the discovery of the action of light in preventing and curing rickets, it would appear that convergence of opinion between the two extreme schools of thought will shortly take place. In any case, modern researches leave no excuse for the continuation of the destructive effects of this terrible disease. As has been stated above, there is already general agreement on the beneficial effects of the administration of cod-liver oil in rickets, so that considerable interest attaches to the efforts to isolate the active substance it contains. The older theories attributed the almost specific action of cod-liver oil to various causes. By some it was held that the minute trace of iodine found in the oil is the active constituent, whilst others believed the therapeutic value to be dependent on the small amounts of nitrogen bases frequently present. A third theory which held ground for a long time regarded the peculiar nature of the unsaturated fatty acids as being responsible for the ease with which the oil can be absorbed and utilised by an ill-nourished system. All these theories are now untenable, since it has been shown that the active substance can be transferred almost without loss to the unsaponifiable fraction of the oil, if precautions are taken to prevent oxidation.[84, 85, 86] This fraction contains no detectable trace of nitrogen or iodine and is of course entirely free from fatty acids.[87]

That the anti-rachitic vitamin and vitamin-A are probably of the same type, if McCollum should be correct in thinking that they are not the same substance, is indicated by the observations of T. F. Zucker, A. M. Pappenheimer, and M. Barnett[88] and of T. F. Zucker and M. B. Gutman.[89] Attempts to fractionate the unsaponifiable material from cod-liver oil by J. C. Drummond and K. H. Coward have as yet yielded no positive information regarding the nature of the vitamin.[87] The origin of the vitamin in cod-liver oil and other fish oils has been studied by J. C. Drummond and S. S. Zilva,[90] who drew the conclusion that the primary source is represented by the marine plant life, chiefly unicellular. The actual synthesis of the vitamin by a typical marine diatom, *Nitszchia closterium,* growing in pure culture in an inorganic medium, was demonstrated by H. L. Jameson, J. C. Drummond, and K. H. Coward,[91] whilst the presence of the growth-promoting factor in

[83] Special Report No. 68, Medical Research Council, 1922.
[84] McCollum and M. Davis, *J. Biol. Chem.*, 1914, **19**, 245.
[85] Steenbock and Boutwell, *ibid.*, 1920, **42**, 131. •
[86] K. H. Coward and J. C. Drummond, *Biochem. J.*, 1921, **15**, 530.
[87] J. C. Drummond and K. H. Coward, *J. Soc. Chem. Ind.*, 1922, **41**, 561 R.
[88] *Proc. Soc. Exp. Biol. Med.*, 1922, **19**, 167.   [89] *Ibid.*, 169.
[90] *Biochem. J.*, 1922, **16**, 518.   [91] *Ibid.*, 482.

such organisms has also been recorded by J. Hjort.[92]   An exhaustive study of the modern methods of the preparation of cod-liver oil satisfied J. C. Drummond and S. S. Zilva that little appreciable loss of vitamin-*A* occurs, unless attempts are made to bleach oils of inferior quality by methods involving oxidation.[93]   These subjects are also arousing considerable interest in agricultural circles.

E. B. Hart, J. G. Halpin, and H. Steenbock [94] have examined the causes of weakness of the legs in chicken and conclude from their investigations that a factor of primary importance in avoiding this trouble is an adequate supply of the vitamins present in cod-liver oil.   R. H. A. Plimmer and J. L. Rosedale,[95] while agreeing that the administration of cod-liver oil is of great value to chicken that are being reared on the intensive system, are inclined to attribute the characteristic tendency to weakness of the legs in such birds to an insufficient supply of vitamin-*B*.

The assimilation of calcium by milking cows has been carefully studied by a group of investigators at the University of Wisconsin, and their results have considerable practical importance.   E. B. Hart, H. Steenbock, C. A. Hoppert, and G. C. Humphrey [96] have found it possible to maintain milking cows in calcium and phosphorus equilibrium when on a ration of alfalfa (lucerne) hay and cereal products, provided that the hay had been cured in a manner which prevented undue exposure to air or sunlight.   When the hay had not been prepared with these precautions,[97] negative calcium balances tended to prevail.   The difference in the effect of the two types of hay is attributed to a difference in the degree of destruction of a vitamin which assists calcium assimilation during the curing process.   On green alfalfa, calcium retention was more marked than when the hays were used.[98]

Lipoids.

The researches of Levene and his colleagues on lecithins continue to clear up various points concerning the structure of these substances.   P. A. Levene and T. Ingvaldsen,[99] and P. A. Levene and H. S. Simms [1] have shown by their studies of liver lecithins that several, possibly four, such compounds exist.   Later investigations

[92] *Proc. Roy. Soc.*, 1922, [*B*], **93**, 440.

[93] *J. Soc. Chem. Ind.*, 1922, **41**, 280т.

[94] *J. Biol. Chem.*, 1922, **52**, 379.

[95] *Biochem. J.*, 1922, **16**, 11.

[96] *J. Biol. Chem.*, 1922, **53**, 21.

[97] *Ibid.*, 1922, **54**, 75.

[98] *Ibid.*, 1922, **53**, 21.

[99] *Ibid.*, 1920, **43**, 359; *A.*, 1920, i, 788.

[1] *Ibid.*, 1921, **48**, 185; *A.*, 1921, i, 842.

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have been concerned with the nature of the fatty acids present in egg-lecithin,[2] brain-lecithin,[3] and kephalin.[4] Comparing the mixed lecithins of liver and those of the egg-yolk, the main difference is seen to lie in the much larger proportion of highly unsaturated fatty acids present in the former substances. The possibility has not yet been adequately considered that the variety of lecithins and the highly unsaturated nature of the fatty acids they contain are due to the part which lecithin probably takes in the transport and intermediate metabolism of fats. Brain lecithin and kephalin were found to contain oleic acid as well as acids in which more than one double bond is present. Of the latter acids, arachidonic acid was detected in the form of its octabromo-derivative or by reduction to arachidic acid. Resolution of Linnert's " sahidin " into several fractions, of which one was lecithin, by S. Fränkel and A. Kass[6] has further simplified the list of lipoids, but in another paper the same authors have made up for the loss by describing a new phosphosulphatide from brain.[7]

. The substance " tethelin," isolated from the anterior lobe of the pituitary gland, by T. B. Robertson,[8] and believed by him to be the growth-promoting principle of that tissue, has been examined by J. C. Drummond and R. K. Cannan,[9] who conclude that the product is an impure mixture of lipoid substances. They were also unable to confirm that tethelin, or indeed the anterior lobe of the pituitary gland itself, has any effect on the growth of mice when administered by the mouth.

J. C. DRUMMOND.

[2] P. A. Levene and I. P. Rolf, *J. Biol. Chem.*, 1922, **51**, 507; *A.*, i, 621.
[3] *Idem, ibid.*, 1922, **54**, 99; *A.*, 1923, i, 11.
[4] *Idem, ibid.*, 91; *A.*, 1923, i, 11.
[5] *Biochem. Z.*, 1910, **24**, 268.
[6] *Ibid.*, 1921, **124**, 216.
[7] *Ibid.*, 206.
[8] *J. Biol. Chem.*, 1916, **24**, 397; *A.*, 1916, i, 350.
[9] *Biochem. J.*, 1922, **16**, 53; *A.*, i, 491.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

WITH one or two possible exceptions, the year 1922 has not been marked by any really outstanding discoveries in the domain of agricultural and plant chemistry. There has, however, been steady progress along the lines already developed; the results of the work of recent years are being sorted out and viewed in proper perspective; many conflicting views and contradictory findings are being reconciled by the increasing realisation of the complexity of the problems involved; thus the ground is being cleared and, one hopes, suitable jumping-off places are being made in preparation for further advances into the unknown country beyond the present frontiers of our knowledge.

In the present Report the results which have been published in the past year will be utilised in an attempt to indicate the relations of the various parts of this branch of chemistry to one another. This can be done most easily and logically by taking the living plant as the point about which all our problems centre, and considering these problems mainly in their bearings on the plant. The normal development of the living plant depends on an adequate supply of the raw materials from which it builds up its tissues, and on the maintenance of conditions favourable to the processes whereby it effects that synthesis. Of these raw materials all save carbon dioxide, and in certain cases nitrogen, are supplied by the soil, which is therefore considered first under the proposed method of treatment of the subject. The conditions obtaining in the soil are then considered in their relation to the growth of the plant, after which the processes whereby the plant constituents are built up from the raw materials obtained from the soil and from the air are discussed. The chemistry of plant products calls for notice in this Report only in its bearings on the mechanism of the vital processes of the plant and on the characterisation of different species by their constituents. The chemistry of the vegetable micro-organisms forms a distinct branch of the subject, except as regards the micro-organisms of the soil, and is dealt with, so far as space allows, in a separate final section of this Report.

Fertilisers, and the more technical aspects of soil work, including soil analysis, are only dealt with incidentally in this Report. These

aspects of the subject are discussed in the Report to the Society of Chemical Industry on " Soils and Fertilisers."

The Soil.

From the point of view of plant nutrition, the most important of the constituents of the soil system is the liquid phase, the so-called " soil solution," the medium from which the roots absorb moisture and nutrient substances. The concentration and composition of this solution are dependent, on the one hand, on the moisture relationships of the soil, and on the other on the nature of the mineral and organic soil constituents, which are subject to attack by purely chemical and by biological agencies. According to modern conceptions, the particles constituting the mineral framework of the soil are coated with a colloidal layer composed in part of the products of weathering of minerals, and in part of the degradation products of organic residues. This colloidal layer exerts a profound influence on the physical, chemical, and biological properties of the soil.

The Soil Colloids.

The organic colloidal matter of the soil is conveniently described as humic matter, although the terms " humus " and " humic acid " now have a more precise significance to the soil chemist : the former term refers to that part of the soil organic matter that is soluble in alkali and precipitated by acids, whilst " humic acid," strictly speaking, consists of that part of the humus that is insoluble in alcohol.

There is considerable controversy in Germany as to the mode of origin and the chemical nature of humic acid, although the question there at issue is the relation of this material to coal formation. Eller and Marcusson [1] have advanced rival theories according to which humic acid is derived from phenolic substances and from furan derivatives, respectively. Marcusson [2] maintains that the humic acids obtained from brown coal contain condensed furan and benzene rings, and that they stand in close relationship to, if they are not identical with, the synthetic acids prepared from sugars. He is supported by Jonas [3] in asserting that Eller's products do not resemble the naturally occurring humic acids, but Eller [4] maintains his position. Schrader has studied the production of humic acid from lignin by alkaline oxidation. [5] The uncertainty of the whole position is really due to the lack of characterisation of

[1] *Ann. Reports,* 1921, **18**, 194.

[2] J. Marcusson, *Z. angew. Chem.,* 1922, **35,** 165; *A.,* i, 436.

[3] K. J. Jonas, *Brennstoff Chem.,* 1922, **3,** 52; *A.,* i, 326.

[4] W. Eller, *ibid.,* **49, 55;** *A.,* i, 326.

[5] H. Schrader, *ibid.,* ii, 161; *A.,* i, 637.

humic acid. The grounds on which the various artificial products are stated to be identical with the natural material are usually far from convincing. Further work on the lines of that of Odén [6] on the humic acid of peat is needed; the problem is at present being studied on these lines in the Rothamsted laboratories. The so-called " ulmin " which forms a principal constituent of dopplerite, a gelatinous deposit found in peat bogs, is probably closely related in nature and in mode of formation to the humic acid of the soil. A suggestive investigation of this material has been carried out in this country. [7]

Whatever may be the mechanism of humification, the resulting product is of great importance in the soil. Its action, which consists partly in modifying the moisture relationships and other physical properties of the soil, has been discussed by the reporter. [8]

The inorganic colloidal matter of the soil, variously known as the " clay " (in this country), the " ultraclay " (in the United States), or the " colloidal clay " (in Germany), consists of the very fine mineral particles of the soil, and of the products of weathering of the soil minerals. From the fact that the smallest clay particle that could be observed by microscopic methods had a diameter of about 0·0001 mm., Whitney [9] has advanced a hypothesis in which the non-observance of particles smaller than this is assumed to be due to the fact that particles of this size contain so few molecules that they are disintegrated by the bombardment of water molecules, leaving the oxides of silicon, aluminium, and iron in colloidal form. It must, however, be pointed out that particles of diameter less than 0·0001 mm. are beyond the resolving power of the microscope, so that their non-observance is no evidence that they do not exist. Gordon [10] disagrees with Whitney's theory, and prefers to regard the process as based on chemical reactions of hydrolysis, etc. To the writer, this discussion seems to be rather beside the mark; if the nature of the products of weathering of soil minerals, and the effect of conditions on the process, can be elucidated, it matters little whether they are produced by bombardment with water molecules, or by hydrolysis, if indeed these do not both mean practically the same thing.

The effect, on the decomposition of minerals, of micro-organisms such as diatoms [11] or bacteria [12] has been investigated.

[6] For example, S. Odén, *Trans. Faraday Soc.*, 1922, **17**, 288.

[7] F. V. Tideswell and R. V. Wheeler, *T.*, 1922, **121**, 2345.

[8] H. J. Page, *Trans. Faraday Soc.*, 1922, **17**, 272.

[9] M. Whitney, *Science*, 1921, **54**, 653; *A.*, i, 708.

[10] N. E. Gordon, *ibid.*, 1922, **55**, 676; *A.*, i, 1227.

[11] W. J. Vernadsky, *Compt. rend.*, 1922, **175**, 450; *A.*, i, 1096.

[12] D. Wright, *Calif. Univ. Pubs. Agric. Sci.*, 1922, **4**, 245.

It has been shown [13] that the values of such physical constants of a soil as density, pore space, water-absorbing power, swelling on moistening, are directly related to the amount of clay or organic matter in the soil.

The flocculation of soils, which has such an important bearing on the moisture relationships, and on tilth, is of course a function of the colloidal matter in the soil. Comber's hypothesis with reference to the flocculation of soils by lime [14] has been developed and strengthened by further work [15]; it seems reasonably certain that the " abnormal " flocculation of clay by calcium salts in the presence of alkali is due to the emulsoid siliceous gel coating around the particles, which masks to a greater or less degree the suspensoid properties of the mineral core. The same hypothesis has been used to explain the difference between what are known in the ceramic industry as " fat " and " lean " clays.[16] A comprehensive study of the flocculation of clay and peat by calcium salts in alkaline solution has also been carried out by Mattson.[17] Clay suspensions, if left undisturbed, frequently show a curious layer formation. This phenomenon has been investigated,[18] and it is stated that in any one layer the particles are of uniform size, and that the space between the layers contains particles uniformly dispersed. From the rate of rise or fall of the layers the size of the particles may be calculated by means of Stokes's law. Clays of different origin and different reaction have been found to have the same isoelectric point.[19] Flocculation has been used as the basis of a method for the determination of colloidal clay in soils [20] and it is claimed that the method is more trustworthy than that based on hygroscopicity measurements.

Absorption and basic exchange, between the soil colloids and the constituents of the soil solution, have an important bearing on the composition and concentration of the latter. Many of the shortcomings of present methods of soil analysis may be ascribed to a lack of sufficient discrimination between that part of the bases of the soil which is absorbed, and therefore capable of liberation by basic exchange, and that part which is actually insoluble, but

[13] B. A. Keen and H. Raczkowski, *J. Agric. Sci.,* 1921, **11**, 441.

[14] *Ann. Reports,* 1920, **17**, 186.

[15] N. M. Comber, *J. Agri. Sci.,* 1921, **11**, 450; *A.,* i, 212; *ibid.,* 1922, **12**, 372; see also *Trans. Faraday Soc.,* 1922, **17**, 349.

[16] N. M. Comber, *J. Soc. Chem. Ind.,* 1922, **41**, 77T.

[17] S. E. Mattson, *Koll. Chem. Beihefte,* 1922, **14**, 227; *A.,* i, 800.

[18] E. Ungerer, *ibid.,* 1921, **14**, 63; *A.,* ii, 96.

[19] O. Arrhenius, *J. Amer. Chem. Soc.,* 1922, **44**, 521; *A.,* i, 707.

[20] R. Sokol, *Internat. Mitt. Bodenkunde,* 1921, **11**, 184.

capable of solution by acids. Hissink [21] has carried out a suggestive investigation on this point, which merits detailed perusal. The present state of our knowledge of absorption and basic exchange in soils has been reviewed by Fisher [22] and by von Nostitz,[23] who has demonstrated how the whole of the readily available potash in a soil may be removed by basic exchange with ammonium nitrate, followed by leaching, so that plants grown on soil so treated show all the symptoms of potash-starvation. The influence of soil colloids and of hydrogen-ion concentration on the availability of calcium, potassium, and phosphates [24] and of ammonium salts [25] has also been investigated.

Biochemical Changes in the Soil.

The composition of the soil solution is influenced not only by the chemical processes of weathering and the like, and by physico-chemical phenomena such as absorption and basic exchange, but also to an even greater extent by the biochemical processes brought about by the plentiful and varied soil microflora and microfauna.

The nitrogen cycle—the complex series of reactions through which the nitrogen compounds of the soil pass—is perhaps of the greatest importance in this connexion. Nitrogen is added to the soil in the form of artificial fertilisers and of plant and animal residues, and by means of biological fixation, whilst it may be lost by leaching, by evolution of gaseous nitrogen, and by absorption by the growing crop. The level at which the nitrogen content of any soil stands depends on the interaction of these factors, which are variously affected by different conditions.[26]

Nitrogen fixation by free-living bacteria in the soil is a factor as to the quantitative importance of which under field conditions there is still some uncertainty. The influence of salts on the process has been investigated [27]; it was found that nitrogen-fixing bacteria were much more resistant to the toxic action of salts than are ammonifiers and nitrifiers, and that many common soil salts had a stimulating action. Boric acid causes increased fixation by *Azotobacter chroococcum* in the presence of humus, although its

[21] D. J. Hissink, *Internat. Mitt. Bodenkunde*, 1922, **12**, 81.

[22] E. A. Fisher, *Trans. Faraday Soc.*, 1922, **17**, 305.

[23] A. von Nostitz, *Mitt. deut. landw. Ges.*, 1921, **36**, 608; *A.*, i, 511; *J. Landw.*, 1922, **70**, 45.

[24] N. E. Gordon and E. B. Starkey, *Soil Sci.*, 1922, **14**, 1; *A.*, i, 1104.

[25] B. Aarnio, *Z. Pflanz. Düng.*, 1922, [A], **1**, 320; *A.*, i, 1227.

[26] For a discussion of this problem see F. E. Bear, *J. Amer. Soc. Agron.*, 1922, **14**, 136.

[27] J. E. Greaves, E. G. Carter, and Y. Lund, *Soil Sci.*, 1922, **13**, 481; *A.* i, 976.

action in absence of the latter is inappreciable. The same is true of its toxic effect in higher concentrations.[28] A new nitrogen-fixing bacillus has been described.[29] The functions of the unicellular green algæ which are present in most soils are not yet known. According to Wann,[30] they can assimilate atmospheric nitrogen; this result, if confirmed, might be of considerable importance in relation to the nitrogen economy of the soil; according to work (as yet unpublished) in the Rothamsted laboratories, however, the question cannot yet be taken as settled.

A moment's reflection will show that in the process of ammonification, whereby the nitrogen of the complex organic material of plant residues and the like is rendered soluble by the action of soil micro-organisms, the initial stages of the action of these organisms must depend largely and probably exclusively on extracellular enzymes, since the complex materials are all insoluble or colloidal, and therefore presumably cannot be absorbed as such into those micro-organisms which feed " osmotically." Several of the bacteria which are most commonly found in the soil have been shown [31] to produce extracellular proteases which were active within a range of hydrogen-ion concentration of p_H 4—9, with an optimum zone of 6 to 7, a zone closely corresponding with the average hydrogen-ion concentration of a fertile soil. Moulds may also be active ammonifying agents; the production of ammonia from protein by the action of *Aspergillus niger* has been investigated.[32] The biological degradation of organic nitrogen compounds in humus forest soils has also been investigated.[33]

Nitrification—the final stage in the chain of reactions whereby organic nitrogen in the soil is rendered available to the plant— is a process requiring an ample supply of air. The physical condition of the soil thus has a direct effect on nitrate formation; this aspect of the subject has received further study.[34] The kinetics of nitrification have also been investigated; [35] the reaction as a whole is found to be an autocatalytic unimolecular reaction, increase in nitric acid being in accordance with the equation :

$$\log x - \log(A - x) = K(t - t').$$

The proportions of the total nitrogen of a soil which are present

[28] J. Voicu, *Compt. rend.*, 1922, **175**, 317.
[29] G. Truffaut and N. Bezssonoff, *ibid.*, 544.
[30] F. B. Wann, *Amer. J. Bot.*, 1922, **8**, 1.
[31] K. G. Dernby, *Biochem. Z.*, 1921, **126**, 105; *A.*, i, 405.
[32] V. S. Butkevitsch, *ibid.*, 1922, **129**, 445; *A.*, i, 707; see also *A.*, i, 973.
[33] H. Suchting, *Z. Pflanz. Düng.*, 1922, **1**, 113.
[34] P. H. Carpenter and A. K. Bose, *Ind. Tea Assoc., Sc. Dept. Quart. J.*, 1921, 103; see also T. L. Lyon, *J. Amer. Soc. Agron.*, 1922, **14**, 97.
[35] K Miyake and S. Soma, *J. Biochem. (Japan)*, 1922, **1**, 123; *A.*, i, 1096.

at any time in the form of soluble nitrate and of insoluble organic compounds depend on the interaction of the various groups of micro-organisms, and on their conditions. Thus it is known that in the presence of an abundance of a non-nitrogenous source of energy, such as carbohydrate, much of the soluble nitrogen in the soil is reassimilated by the soil organisms and thus locked up for a time in a form in which it is not available to the plant. The effect of a straw mulch in depressing the nitrate content of the soil has been investigated.[36] This depression is greatest when the soil is at its wettest after rain; and it seems probable that this result is to be explained by the washing down into the soil of soluble decomposition products of the straw, which would then exert the action above mentioned.[37]

The sulphur cycle has received a considerable amount of attention of recent years. The reduction of sulphates to sulphides under anaërobic conditions, such as obtain in deep subsoils, has been found to occur in depths from 10 metres to 34·5 metres in the Amsterdam district.[38] The organism operative in this process is *Microspira desulphuricans*. Sulphides are similarly found in the lower layers of peat soils.[39] Under aërobic conditions, on the other hand, sulphate formation occurs. Demolon[40] has studied the sulphur-oxidising power of soils and concludes that the ammonifying organisms are apparently responsible, and that the property is not bacteriologically specific. Sulphur-oxidation has, however, received most attention at the New Jersey Experiment Station, by J. G. Lipman and his co-workers. Two specific organisms, *Thiobacillus thio-oxydans* and *Thiobacillus B.*, have been isolated;[41] the former, which acts best in acid media, is not commonly found in cultivated soils, except after treatment with sulphur; the latter, which acts in alkaline solution, appears to be closely related to Beijerinck's *Thiobacillus thioparus*, and is commonly present in cultivated soils in America, especially " black alkali " soils. *Thiobacillus thio-oxydans* is an extraordinary organism; its optimum growth occurs at a hydrogen-ion concentration of p_H 2·8—2·0, and it can exist in a medium of p_H 0·58.[42] It is auto-

[36] W. A. Albrecht, *Soil Sci.*, 1922, **14**, 299.

[37] See also J. A. Bizzell, *J. Amer. Soc. Agron.*, 1922, **14**, 320.

[38] C. A. H. von Wolzogen Kühr, *Proc. K. Acad. Wetensch. Amsterdam*, 1922, **25**, 188; *A.*, i, 1228.

[39] C. O. Rost, *Soil Sci.*, 1922, **14**, 167.

[40] A. Demolon, *Compt. rend.*, 1921, **173**, 1408; *A.*, i, 312.

[41] S. A. Waksman, *J. Bact.*, 1922, **7**, 231, 605, 609; *Soil Sci.*, 1922, **13**, 329; *A.*, i, 706; S. A. Waksman and J. S. Joffe, *J. Bact.*, 1922, **7**, 239; J. S. Joffe, *Soil Sci.*, 1922, **13**, 161.

[42] J. G. Lipman, S. A. Waksman, and J. S. Joffe, *Soil Sci.*, 1921, **12**, 475; *A.*, i, 303.

trophic, utilising sulphur as a source of energy, and assimilating carbon dioxide. It has also been found that certain bacteria can oxidise zinc blende to zinc sulphate.[43]   Lantzsch concludes, from an investigation into the various phases of the sulphur cycle, that " the sulphur cycle in soil does not justify the assumption that free sulphuric acid is produced (directly or via hydrogen sulphide) and exerts a solvent action.   An increase of soil acidity is obtained only with heavy dressings of sulphur." [44]   The bearings of sulphur-oxidation on the soil reaction and on crop production are discussed later in this Report.

Lantzsch [45] also suggests the possibility of a direct connexion between nitrification and the solubility of the phosphates of the soil, inasmuch as it is stated that the seasonal maxima of nitrate content of the soil coincide with maxima for the phosphate content of the soil solution.

Soil Moisture and the Soil Solution.

The moisture relationships of the soil, which are so dependent on the amount of colloidal matter present, themselves have a direct bearing on the strength of the soil solution, inasmuch as the extent to which the latter may be subject to dilution or concentration varies with the moisture-holding capacity of, and rate of evaporation of water from, the soil.   It has been found that the absorption of water by the colloidal matter extracted from a number of widely different American soils was relatively constant.[46]   Odén has published a suggestive note on the hygroscopicity of clay.[47]   The rate of evaporation of water from a soil receiving farmyard manure every year, and therefore relatively rich in colloidal organic matter, is less than that from unmanured soil or from soil receiving only artificial fertilisers.[48]   The evaporation of water from soil in the field has been investigated by Helbig and Rössler.[49]   Evaporation of water from the soil tends to cause an accumulation of soluble salts in the surface layers of the soil.   This takes place, as would be expected, during the summer months, especially in a dry summer, and is most pronounced in the top quarter of an inch of the soil.[50] In this investigation the concentration of soluble salts was deter-

[43] A. Helbronner and W. Rudolfs, Compt. rend., 1922, 174, 1378; A., i, 706.

[44] K. Lantzsch, Internat. Mitt. Bodenkunde, 1922, 12, 22.

[45] K. Lantzsch, loc. cit.

[46] W. O. Robinson, J. Physical Chem., 1922, 26, 647; A., i, 1228; see also R. O. E. Davis, J. Amer. Soc. Agron., 1922, 14, 293.

[47] S. Odén, Trans. Faraday Soc., 1922, 17, 244.

[48] B. A. Keen, J. Agric. Sci., 1921, 11, 433.

[49] M. Helbig and O. Rössler, Z. Pflanz. Dung., 1922, 1, 95.

[50] C. E. Millar, Soil Sci., 1922, 13, 433.

mined by the freezing-point method, which has been extensively studied by Bouyoucos. This worker concluded [51] from freezing-point and dilatometer measurements that a portion of the soil moisture was "unfree," and inactive as a solvent. Parker now presents evidence [52] that Bouyoucos's assumptions are not well founded, and that soils do not contain a considerable percentage of water which does not act as a solvent. Although the old classification of soil moisture into hygroscopic, capillary, and gravitational water has certain objections, it seems to be the best yet offered. Keen [53] has published a useful general discussion of modern views on the moisture relationships of the soil.

As an alternative to the examination of the soil solution *in situ*, several methods have been devised for isolating it from the soil. These methods fall into several categories, one of which is the application of very high pressures to the moist soil. This method was used in California by C. B. Lipman, and it has now been developed in the same laboratory by Burgess [54] who by the application of pressures up to 16,000 lb. per square inch has succeeded in expressing from soils at a moisture content of 50 per cent. of their moisture-holding capacity, between 45 and 60 per cent. of their total moisture. By an examination of the composition of the liquid so expressed, and comparison with a 1 : 5 water extract, it is concluded that the liquid obtained by the direct pressure method does represent the true soil solution, and further, that the balance of evidence is against the existence of "unfree" water, thus confirming Parker's conclusions. [55]

In the reporter's opinion, there is still some reason to doubt whether any of the methods for isolating the soil solution are really capable of doing so, at any rate for heavy soils, in which the amount of colloidal matter is high. These methods are usually most successful with coarse soils, in which it is not difficult to suppose that a large part of the soil solution may be regarded as existing as a free water film on the surface of the comparatively bare mineral grains. For heavy soils much greater difficulties are encountered, as noticed by Burgess [56] with the Parker displacement method, and this is confirmed by experience of the same method in the Rothamsted laboratories. In such soils it must be supposed that the soil solution is to a large extent imbibed in the capillary channels of the compound particles, and in the hydrophilous gel

[51] *Ann. Reports*, 1921, **18**, 200.

[52] F. W. Parker, *Soil Sci.*, 1922, **13**, 43; *A.*, i, 116.

[53] B. A. Keen, *Trans. Faraday Soc.*, 1922, **17**, 228. For " Wilting point " see also W. L. Power, *Soil Sci.*, 1922, **14**, 159.

[54] P. S. Burgess, *Soil Sci.*, 1922, **14**, 191.

[55] F. W. Parker, *loc. cit.*   [56] P. S. Burgess, *loc. cit.*

coating of the particles; it will therefore be more difficult to remove than that in a coarse soil containing little colloidal matter, and in a displacement method the possibility of dilution by the displacing liquid will be considerable. The degree of hydration of the gel coating on the particle is doubtless much greater on the outside than towards the surface of the mineral " core." If this is so, it follows that by any method in which an attempt is made to remove the soil solution from the soil, a part of this solution will be removed with greater ease than the rest; if at the same time it is assumed —and there appears to be some grounds for the assumption—that there is a concentration gradient in the soil solution as between the outside and the inner layers of the gel coating of the particles, then it would follow that the first portions of the expressed soil solution would have a different concentration from that of the portions removed later. . This is not found for relatively coarse soils, but there is some indication of it in Burgess's results [56] for soils containing a fair amount of clay. The concentration of the true soil solution could then only be expressed as a mean value, represented possibly by that of a portion of the solution collected when about half of the original soil moisture had been isolated from the soil.

The reaction of the soil solution continues to provoke a bigger volume of work than practically any other soil problem. Much confusion has resulted in this field from the fact that " soil acidity " is a complex phenomenon, in the development of which several distinct factors are involved; these have not always been clearly distinguished. Lemmerman and Fresenius [57] emphasise this point, and distinguish three types of soil acidity : (1) actual acidity of the soil solution, due to the presence of acids; (2) latent acidity, developed in the presence of neutral salts, owing to the liberation, by basic exchange, of readily hydrolysed iron and aluminium salts; (3) latent acidity, developed in the presence of salts of weak acids with strong bases, the base being absorbed by the soil colloids and the acid left. The measurement of the hydrogen-ion concentration of the soil solution [58] does not necessarily give any indication of the amount of base required to bring about neutrality; this is determined partly by the buffer action of some of the soil constituents,[59] and partly by the fact that some of the base is precipit-

[56] P. S. Burgess, *lot. cit.*

[57] O. Lemmermann and L. Fresenius, *Z. Pflanz. Düng.*, 1922, [*A*], **1**, 12; *A.*, i, 510.

[58] See, for example, D. J. Healy and P. E. Kanaker, *Soil Sci.*, 1922, **13**, 323; *A.*, i, 519.

[59] E. A. Fisher, *Nature*, 1921, **108**, 306; *A.*, i, 510; H. W. Johnson, *Soil Sci.*, 1922, **13**, 7; *A.*, i, 708.

ated or absorbed by the soil colloids. Calcium hydroxide and bicarbonate are involved in this latter effect to different extents; this helps to explain the different "lime-requirement" values given by the use of these two reagents.[60] The titration curve obtained by measuring the rate of change of hydrogen-ion concentration on the gradual addition of acids and alkalis gives valuable information as to the magnitude of the buffer effects in a soil, which will determine to what extent the latent acidity of the types specified under (2) and (3) above can produce harmful effects in the soil.[61] A well-buffered soil is more productive than a badly buffered one; clay soils are better buffered than sandy soils.[62] The relation of the soluble iron or aluminium of the soil to soil acidity forms the basis of Comber's qualitative test,[63] now described in a modified form;[64] a "lime-requirement" method based on this test has been described.[65] It is usually supposed that acidity may be caused by the presence of aluminium salts owing to their ready hydrolysis. It is now suggested, however, that the presence of soluble aluminium salts in soils is the result rather than the cause of soil acidity.[66] It seems likely that the first explanation may be correct in some cases, as in case (2) above, and the second in other cases, as, for instance, when mineral acid is produced in the soil by the use of " physiologically acid " fertilisers like sulphate of ammonia, or by the oxidation of sulphur. Crowther[67] has published a review of the physico-chemical aspects of soil acidity.

The use of the bacterial oxidation of sulphur as a means of increasing the hydrogen-ion concentration of the soil continues to attract much attention in America. Potato scab disease can be controlled by treating the soil with sulphur inoculated with *Thiobacillus thio-oxydans*, the acidity produced by the oxidation of the sulphur being sufficient to inhibit the growth of *Actinomyces scabies*, the organism responsible for the disease.[68] Similarly, the alkalinity of " black alkali " soil can be reduced by treatment

[60] V. Vincent, *Compt. rend.*, 1922, **175**, 1233.

[61] E. A. Fisher, *loc. cit.*; see also C. H. Spurway, *Michigan Agric. Exp. Sta., Technical Bull.* No. 57; October, 1922.

[62] O. Arrhenius, *loc. cit.*, and *Soil Sci.*, 1922, **14**, 223.

[63] *Ann. Reports*, 1920, **17**, 178; see also J. Hudig and C. W. G. Hetterschij, *Chem. Weekblad*, 1922, **19**, 366; *A.*, i, 1104.

[64] N. M. Comber, *J. Agric. Sci.*, 1922, **12**, 370.

[65] R. H. Carr, *J. Ind. Eng. Chem.*, 1921, **13**, 931; *A.*, i, 172.

[66] I. A. Denison, *Soil Sci.*, 1922, **13**, 81; *A.*, i, 512.

[67] E. M. Crowther, *Trans. Faraday Soc.*, 1922, **17**, 317.

[68] S. A. Waksman, *Soil Sci.*, 1922, **14**, 61; see also W. H. Martin, *ibid.*, 1921, **11**, 75.

with inoculated sulphur, although it is also necessary to leach out the salts if the full benefit is to be obtained.[69]

The Effect of Soil Conditions and of Fertilisers on Plant Growth.

In the first section of this Report, the work of the past year has been considered in relation to the influence of the various soil factors on the soil solution; in this section, the relation of the soil solution to the growth of the plant will be discussed.

The effect of the concentration of the soil solution on plant growth is a question which is at present but little understood.   The usually accepted view is that the plant root absorbs nutrient ions from the soil solution by osmosis.   On this view, there will probably be for any plant a *minimum* concentration for each ion, below which the plant is unable to absorb that ion.   The minimum value will vary for different ions and for different plants.   The lack of knowledge as to the values of these minima is partly responsible for the difficulty of interpreting the results of soil analysis in terms of soil fertility.   Vesterberg [70] has discussed this point, and from an examination of various data he has put forward tentative average values for these minima for nitrogen, potash, and phosphate.   When the requirements of any plant have been ascertained, it will then be necessary to find, for any given soil, (1) whether it can give the required concentration in the soil solution and (2) whether it can maintain it.   Comber,[71] however, advances an interesting modification of the present osmotic hypothesis of the mechanism of root absorption in the soil.   He maintains that the assumption that plants feed in the soil just as they feed in water cultures is unjustified and contrary to the facts.   He adduces evidence in favour of the view that colloids can be directly absorbed by the plant, and advances the hypothesis that there is a direct union of the root hair with the particles of the soil; this union is brought about by colloidal mucilaginous matter from the cell wall of the root hair on the one hand, and the hydrophilous gel coating around the soil particle on the other, which intermingle to form one system, thereby enabling the direct absorption of colloids, and permitting the acid juices of the plant cell to attack directly the particles of the soil. The acceptance of this hypothesis would, of course, necessitate a radical reconsideration of our views regarding the relation of the soil solution to the plant.

The effect of the composition of the soil solution on plant growth

[69] W. Rudolfs, *Soil Sci.*, 1922, **13**, 215.

[70] K. A. Vesterburg, *Internat. Mitt. Bodenkunde*, 1922, **12**, 11.

[71] N. M. Comber, *J. Agric. Sci.*, 1922, **12**, 363.

may next be considered. Besides the ammonium salts and nitrates produced by biological agencies in the soil, it is concluded from a study of the action of alkaline permanganate that the nitrogen present in the soil as amino-acids, and part of that present as acid amides, are immediately available.[72] It is doubtful, however, whether such substances are normally present in sufficient amount to be of importance.

Some American soils seem to be actually deficient in sulphates, so that they give increased crops by treatment with sulphur.[73] For this treatment to be successful, the dressings must be small, otherwise if the oxidising power of the soil is high and the soil not well buffered, the hydrogen-ion concentration is increased to a point at which the plant suffers.[74]

The utilisation of phosphates varies for different species of plants, and appears to bear a direct relation to the ratio $CaO : P_2O_5$ in the ash of the plant.[75] Ammonium humate or colloidal humic acid is stated to increase the solubility of mineral phosphates and thus to give rise to increased phosphate assimilation.[76] It is also stated that the same effect is obtained by the active nitrification of urea,[77] thus supporting the suggestion of Lantzsch.[78] It is not practicable to render mineral phosphates more soluble by direct application of sulphur to the soil, since the hydrogen-ion concentration required to effect the transformation (p_H 3·1—2·8) is harmful to plants.[79] In the Rothamsted field experiments, it has long been found that increased yields are obtained on phosphate-deficient soil by the application of sodium silicate, and it is usually supposed that this effect is due to increased assimilation of phosphate in the presence of silica. Lemmermann and Wiessman [80] have obtained similar results in pot experiments using colloidal silica, but they obtained significant increases also in the complete absence of phosphates, from which they conclude that colloidal silica has a

[72] C. S. Robinson, O. B. Winter, and E. J. Millar, *J. Ind. Eng. Chem.*, 1921, **13**, 933; *A.*, i, 212.

[73] See, for example, F. C. Reimer and H. V. Tartar, *Oregon Agric. Exp. Sta., Bull.*, 163, 1919; also J. Woodard, *Bot. Gaz.*, 1922, **73**, 81.

[74] W.Rudolfs, *Soil Sci.*, 1922, **14**, 247; see also J. S. Joffe and H. C. McLean, *ibid.*, 217. For German experience see B. Heinze, *Z. Pflanz. Düng.*, 1922, [*A*], **1**, 154; E. Kruger, *ibid.*, 166; Gerlach, *Mitt. Deut. landw. Ges.*, 1921, **36**, 726.

[75] M. von Wrangell, *Landw. Jahrb.*, 1922, **57**, 1; *A.*, i, 1098.

[76] K. Mack, *Chem. Ztg.*, 1922, **46**, 73.

[77] J. S. Marais, *Soil Sci.*, 1922, **13**, 355.

[78] K. Lantzsch, *loc. cit.*

[79] W. Rudolfs, *loc. cit.*

[80] O. Lemmermann and H. Wiessmann, *Z. Pflanz. Düng.*, 1922, [*A*], **1**, 185; *A.*, i, 1103.

direct effect on plant growth, and that it acts in the presence of phosphate deficiency by virtue of an ability partly to replace phosphate in the plant. They do not appear, however, to have determined the amounts of phosphate and silica taken up by the increased crops; this would throw light on the relative importance of the supposed direct action of the silica on the plant and of its possible indirect action in causing increased assimilation of phosphates. Shedd [81] has also obtained increased growth by the application of silica.

One of the effects of potash on the plant is to increase its vigour, and its resistance to disease. This is well instanced by a result reported from Arkansas; [82] on a control plot receiving no potash, 95 per cent. of the cotton plants died from the wilt disease, whereas on the plot receiving kainit not a single plant was affected.

Experiments in Kentucky [83] indicate that some soils may be deficient in calcium, and that by the application of salts of this metal, crop increases may be obtained which are not due merely to decreased hydrogen-ion concentration.

The effect of the reaction of the soil solution on plant growth is gradually being elucidated. Sour soils are recognised agriculturally by well-defined symptoms, such as the growth of certain characteristic weeds, the liability of cruciferous crops to " finger and toe " disease, and the failure of most leguminous crops. It does not follow, however, that a soil which is " acid " according to chemical tests is " sour " in the agricultural sense; the hydrogen-ion concentration which is definitely harmful varies greatly for different crops, [84] and under undisturbed natural conditions the character of the flora may be largely influenced by the reaction of the soil solution. [85] Most common crop plants appear to be unaffected by, and even possibly to prefer, a faintly acid medium. Thus it has been shown [86] that although peas, maize, wheat, oats, and carrots all germinated most slowly at hydrogen-ion concentrations of p_H 5—6, root growth after ten days was at a maximum between these values, which are regarded as representing the values for normal growth. There is always a tendency, when a plant is

[81] O. M. Shedd, *Soil Sci.*, 1922, **14**, 233.

[82] L. E. Rast, *J. Amer. Soc. Agron.*, 1922, **14**, 222.

[83] O. M. Shedd, *loc. cit.*, and *Kentucky Agr. Exp. Sta. Bull.*, 236 (1921); *A.*, ii, 527.

[84] See, for example, O. Lemmermann and L. Fresenius, *loc. cit.*

[85] E. J. Salisbury, *Ann. Bot.*, 1922, **36**, 391; *A.*, i, 1104; W. R. G. Atkins, *Nature*, 1921, **108**, 80; *A.*, i, 415; *Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 369; *A.*, i, 509; A. P. Kelley, *Soil Sci.*, 1922, **13**, 411; C. Olsen, *Science*, 1921, **54**, 539.

[86] R. M. Hixon, *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 91; *A.*, i, 1221; see also O. Arrhenius, *J. Gen. Physiol.*, 1922, **5**, 81; *A.*, i, 1097.

growing in a solution with a hydrogen-ion concentration towards one extreme, for the plant to modify this value towards one lying between p_H 5·0 and 6·8. The cell-sap of many plants is acid,[87] and it has been found that plants may tend to alter the acidity of the soil solution so as to bring it closer to that of their own root sap.[88] On the other hand, the acidity of the plant juices may be directly influenced by that of the soil solution.[89] The harmful effect of sour soils may often be due not so much to the acidity of the soil solution as to the soluble iron and aluminium compounds they contain.[90] Soil acidity may also affect soil fertility indirectly by its deleterious effect on many of the micro-organisms concerned in the nitrogen cycle. Thus nitrification is hindered by acidity : a case is reported where a strong nitrite reaction developed in a soil at p_H 3·9—4·4,[91] whilst in another instance, it was found that those acid soils which responded to lime in the field were the ones in which lime treatment caused a rapid formation of nitrates.[92] Growth of, and nitrogen fixation by, *Azotobacter* are inhibited by acidity higher than p_H 5·9—6·0.[93]

The effect of partial sterilisation of the soil by arsenates and arsenites [94] and by various aromatic substances [95] has been studied.

Russell and Hutchinson's view of the mechanism of partial sterilisation is that the sterilising agent kills off the soil protozoa, which normally limit the numbers of beneficial bacteria in the soil, and thus enables the latter to attain greatly increased numbers and to produce increased quantities of plant nutrients.[96] Much discussion has centred round this hypothesis. From an experiment at Rothamsted in which the numbers of active amoebæ and of bacteria in a field soil were counted daily for 365 days, it has been clearly established that there is a definite inverse relationship

[87] See, for example, W. R. G. Atkins, *Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 414; *A.*, i, 411.

[88] J. König, J. Hasenbäumer, and E. Kröger, *Z. Pflanz. Düng.*, 1922, [*A*], **1**, 3; *A.*, i, 510.

[89] F. C. Bauer and A. R. C. Haas, *Soil Sci.*, 1922, **13**, 461; *A.*, i, 975.

[90] S. D. Conner and O. H. Sears, *ibid.*, 23; *A.*, i, 613; N. M. Comber, *Nature*, 1921, **108**, 146; *A.*, i, 416; C. H. Arndt, *Amer. J. Bot.*, 1922, **9**, 47; *A.*, i, 1103.

[91] F. C. Gerretsen, *Arch. Suikerindus. Nederland-Indie*, 1921, **29**, 1397; *Exp. Sta. Rec.*, 1922, **47**, 214.

[92] R. H. Robinson and D. R. Bullis, *Soil Sci.*, 449; *A.*, i, 976.

[93] P. L. Gainey and H. W. Batchelor, *Science*, 1922, **56**, 49; *A.*, i, 1096.

[94] G. Rivière and G. Pichard, *Compt. rend.*, 1922, **174**, 493; R. Ciferri, *Coltivatore*, 1922, Nos. 32—34.

[95] T. Parker, A. W. Long, and J. S. Mitchell, *Bull. Bur. Bio-Tech.*, 1922, No. 5, 134.

[96] E. J. Russell and H. B. Hutchinson, *J. Agric. Sci.*, 1909, **3**, 111; 1913, **5**, 152.

between the numbers of these two types of organisms : when the numbers of active amœbæ are high, those of the bacteria are low, and vice versa; [97] these results lend very considerable support to Russell and Hutchinson's hypothesis, and show that however many factors there may be which play a part in partial sterilisation, the elimination of the protozoa by the process is by no means the least important.

The relation of crop yield to amount of fertiliser used, and Mitscherlich's application thereto of the " law of minimum " still provoke controversy in Germany.[98]　The question is of considerable practical importance, particularly at a time of agricultural depression such as the present.　There are now some indications [99] that at first increasingly large crop increments may be obtained by successive equal increases in the amount of fertiliser used, and that only with relatively large dressings does the " law of diminishing returns " come into play; the curve for the relation of yield to amount of fertiliser appears to be sigmoid rather than logarithmic in form.

The Chemistry of Plant Processes.

Having discussed the soil and the influence on plant growth of soil factors, including the nutrient materials derived from the soil, it remains to deal with the processes going on within the plant itself.

Carbon Assimilation.

The striking investigations of Baly and his co-workers on the photocatalytic mechanism of the photosynthesis of carbohydrates [1] have now been extended to the production of nitrogen compounds; [2] this work is discussed later in this section.　The photoelectric properties of chlorophyll, and their bearing on the electronic theory of sensitisation, have received further attention.[3]　The energy changes accompanying carbon-dioxide assimilation (by the green alga, *Chlorella vulgaris*) in artificial light, and the percentage utilisation of energy in different parts of the spectrum have been studied.[4]

[97] D. W. Cutler, L. M. Crump, and H. Saudon, *Phil. Trans.,* 1922, [B], **211,** 317.

[98] E. A. Mitscherlich, *Landw. Versuchs-Stat.,* 1922, **99,** 133; A. Rippel, *J. Landw.,* 1922, **70,** 9.

[99] E. J. Russell, *J. Min. Agric.,* 1922, **29,** 752, 836.

[1] E. C. C. Baly, I. M. Heilbron, and W. F. Barker, *T.,* 1921, **119,** 1025; see also E. C. C. Baly, *J. Soc. Dyers & Col.,* 1922, **38,** 4; *A.,* i, 307.

[2] E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *T.,* 1922, **121,** 1078.

[3] H. H. Dixon and N. G. Ball, *Sci. Proc. Roy. Dubl. Soc.,* 1922, **16,** 435; *A.,* ii, 248.

[4] O. Warburg and E. Negelein, *Z. physikal. Chem.,* 1922, **102,** 235; *A.,* i, 1097; C. Müller and O. Warburg, *Ber. Physikal.-Tech. Reichsanst.,* 1920, *A.,* i, 411.

Kostytschev has published a series of investigations [5] on photosynthesis. He finds that the ratio CO_2/O_2 is disturbed in atmospheres containing abnormally large amounts of carbon dioxide, being first greater and then less than unity. In such atmospheres, leguminosæ assimilate markedly more carbon dioxide than other plants do. Assimilation is increased by the presence of nitrates in the soil. It has been shown that leaves of *Tropæolum majus* can assimilate formaldehyde vapour.[6] The supposed formation of hydrogen peroxide in the assimilation of carbon dioxide by plants [7] could not be confirmed,[8] neither could the statement [9] that leaves floating on sugar solution in sunlight are able to synthesise phloroglucinol be substantiated.[10] The possibility of obtaining substantial crop increases by artificial enrichment of the atmosphere by carbonic acid, which has aroused so much interest in Germany,[11] demands for its successful realisation that due regard be paid to the other controlling factors such as light, moisture, etc.[12]

Carbohydrate Metabolism and Translocation.

The disappearance of starch from leaves kept in the dark is favoured by dry conditions, and results in the production of non-reducing substances.[13] In the case of *Tropæolum majus*, sucrose seems to be the product formed.[14] The leaves of *Fagus sylvatica* and *Æsculus Hippocastanum*, however, when they turn yellow and die, suffer a diminution in their content of soluble carbohydrate, and an increase in their insoluble but readily hydrolysed carbohydrate.[15] From an investigation of the changes and movements of carbohydrates in *Mercurialis perennis* during its annual growth, it is concluded that there is another dextrorotatory substance present in addition to sucrose, though attempts to isolate it have so far failed.[16] The changes in the pectic constituents of apples during the ripening process have been investigated.[17] Soluble pectin is at a maximum when the fruit is ripe.

[5] G. Kostytschev, *Ber. Deut. bot. Gaz.*, 1921, **39**, 319, 328, 334; *A.*, i, 307, 308; *ibid.*, 1922, **40**, 112; *A.*, i. 613.

[6] M. Jacoby, *Biochem. Z.*, 1922, **128**, 119; *A.*, i, 502.   [7] *A.*, 1918, ii, 107.

[8] H. Molisch, *ibid.*, 1921, **125**, 257; *A.*, i, 411.

[9] Waage, *Ber. Deut. bot. Ges.*, 1890, **8**, 250; *A.*, 1891, 605.

[10] M. Nierenstein, *Nature*, 1920, **105**, 391.

[11] *Ann. Reports*, 1921, **18**, 209.

[12] Densch, *Z. Pflanz. Düng.*, 1922, **1**, 32.

[13] H. Molisch, *Ber. Deut. bot. Ges.*, 1921, **39**, 339; *A.*, i, 309.

[14] H. Schroeder and T. Horn, *Biochem. Z.*, 1922, **130**, 165; *A.*, i, 906.

[15] R. Combes and D. Kohler, *Compt. rend.*, 1922, **175**, 590; *A.*, i, 1222.

[16] P. Gillot, *J. Pharm. Chim.*, 1922, [vii], **26**, 250; *A.*, i, 1101.

[17] M. H. Carré, *Biochem. J.*, 1922, **16**, 704; *A.*, i, 1222; see also M. H. Carré and D. Haynes, *ibid.*, 60; *A.*, i, 401.

The quantitative investigation of the movements and changes of carbohydrates in plants would be much facilitated by the discovery of a quick and trustworthy method of starch estimation. A method which promises to satisfy these requirements has been described.[18]

Nitrogenous Assimilation and Metabolism.

Very suggestive results have been obtained by Baly, Heilbron, and Hudson [19] in an extension of their work on photocatalysis to the formation of nitrogen compounds. Setting out from the observation of Schimper [20] that nitrites are always present in the living leaf in the dark, but that they disappear when the leaf is in the light, provided chlorophyll is present; and from the observation of Baudisch [21] that formhydroxamic acid is formed when an aqueous solution of potassium nitrite containing methyl alcohol is exposed to ultra-violet light, these investigators have shown that activated formaldehyde—such as is produced by the action of ultra-violet light of very short wave-length ($\lambda = 200 \ \mu\mu$) on an aqueous solution of carbon dioxide, or of ordinary light on a similar solution containing a photocatalyst such as chlorophyll— readily combines with potassium nitrite to give formhydroxamic acid, which can at once react with more molecules of activated formaldehyde to produce a great variety of complex substances, such as are found in the living plant. These reactions take precedence of the photocatalytic polymerisation of activated formaldehyde to form reducing sugars; the latter only occurs when the activated formaldehyde is produced at a rate greater than that at which it can react with potassium nitrite and with the formhydroxamic acid thus formed. These investigators have no doubt that formhydroxamic acid marks the first stage in the photosynthesis of the nitrogen compounds found in the plant. The reaction may be formulated thus :

$$\text{H-C-OH} + \text{O}{=}\text{N-OK} = \begin{matrix} \text{H---C---OH} \\ \text{O}{=}\text{N---OK} \end{matrix} = \begin{matrix} \text{H---C---OH} \\ \text{N---OK} \end{matrix} + \text{O}$$

Activated   Formhydroxamic acid
formaldehyde.   (potassium salt).
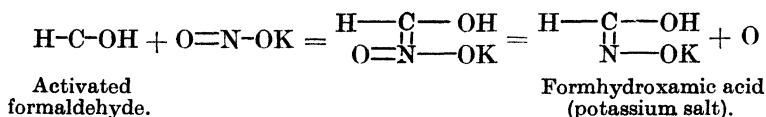
They have obtained definite evidence of the formation of α-amino-acids, of a crystalline alkaloidal base, of a crystalline base closely resembling and possibly identical with glyoxaline, and of a sub-

[18] A. R. Ling, *J. Inst. Brewing*, 1922, **28**, 838; *A.*, ii, 879.
[19] E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *loc. cit.*
[20] Schimper, *Bot. Z.*, 1888, **46**, 65.
[21] Baudisch, *Ber.*, 1911, **44**, 1009. For a recent summary of Baudisch's work, see *J. Biol. Chem.*, 1921, **48**, 489; *A.*, i, 194.

stituted α-amino-acid which may be histidine. They show how the production of these, and of other nitrogenous plant products, by the interaction of activated formaldehyde and formhydroxamic acid, is readily explicable. The following scheme is put forward by them with some confidence as an indication of the main lines along which this photosynthesis takes place :

```
Potassium nitrate              Carbonic acid.
      ↓                              ↓
Potassium nitrite          Activated formaldehyde
      |                              ↓
      ↓_____↓    ↓ --------     --↓
      ↓                              |         Hexoses
      Formhydroxamic acid            |
            ↓                        ↓
            ↓_____↓_____
                     ↓
            Nitrogen bases        α-Amino-acids
•       ↓_____|_____↓       |
   ↓                           ↓         |
Alkaloids and xanthine         ↓_____↓
    derivatives          Substituted α-amino-acids
                              (Histidine, etc.)
                                 ↓
                             Proteins
```
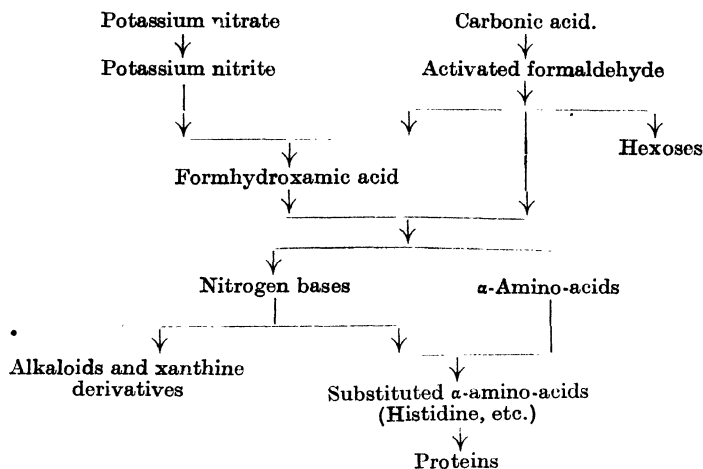
The far-reaching importance of this work can best be emphasised by the following quotation : [22]

" The activated formaldehyde produced by the photocatalytic action of chlorophyll on carbonic acid combines with the potassium nitrite known to be present in the leaves, this reaction taking precedence of all others. The formhydroxamic acid then condenses with more activated formaldehyde, this reaction taking second place in the order of precedence, whilst all excess of the activated formaldehyde polymerises to form hexoses.

" The interaction of the activated formaldehyde with formhydroxamic acid follows two main lines, the formation of aminoacids and of various nitrogen bases. These nitrogen bases consist of various types, namely, pyrrole, pyridine, and glyoxaline, which by further condensation with activated formaldehyde give indole, quinoline, isoquinoline, and xanthine derivatives. In cases where such is possible these bases condense with the amino-acids to give the substituted amino-acids such as histidine, tryptophan, etc. The excess of nitrogen bases undergoes further condensation to give alkaloids, whilst the substituted amino-acids interact to give proteins. The readiness with which all these reactions take place is due to the cardinal fact that the various compounds are produced

[22] E. C. C. Baly, I. M. Heilbron, and D. P. Hudson, *loc. cit.*, p. 1087.

in highly reactive phases, analogous to the highly reactive phase of formaldehyde when photosynthetically formed. This reactivity enables condensations to occur which are otherwise impossible to realise in the laboratory. It is a matter of common knowledge that these reactions must occur in the living plant, and our results show that the key to the problem is the enhanced reactivity of freshly synthesised molecules. . . . The synthesis of the nitrogen compounds found in the plant is not photosynthetic except in so far as the production of the activated formaldehyde by the chlorophyll is concerned. The various amino-acids, proteins, alkaloids, etc., are natural and indeed inevitable results of the photosynthesis of formaldehyde in the presence of potassium nitrite. . . .

". . . . A further conclusion of importance is that the region where the synthesis occurs must necessarily be restricted to the leaves. Since it must not be forgotten that the synthesis of hexoses is taking place concurrently, the conditions are perfect for the formation of glucosides and we believe that the products of the nitrogen synthesis are translocated as soluble glucosides. The fact that nitrogen derivatives are found in other parts of the plant cannot be accepted as an argument that they must have been synthesised in those parts. There can be no doubt that the synthesis takes place in the leaves and that the compounds are subsequently distributed as soluble glucosides by the normal translocatory processes."

Ever since the classical experiments of Boussingault and of Lawes and Gilbert, it has been generally accepted that green plants are entirely dependent for nitrogen on the supplies they receive through their roots in the form of nitrates, ammonia, and possibly other forms, and that none can assimilate the elemental nitrogen of the air, although the leguminous plants are able to live in symbiosis with a nitrogen-fixing bacillus, and therefore are able to live without combined nitrogen from other sources. From time to time the claim has been advanced that green plants *are* able to fix nitrogen, but the evidence has never been free from suspicion. During the past year two further claims have been advanced, both from America. As already mentioned, one of these,[23] on behalf of the unicellular green algæ, is open to question. The other claim is on behalf of that possibly most investigated of all agricultural plants, the wheat plant. Only a preliminary note has so far appeared [24] and details will be awaited with great interest. Whilst no one would lightly deny the *possibility* of nitrogen fixation by green plants, the great bulk of agricultural experience is against

[23] F. B. Wann, *loc. cit.*
[24] C. B. Lipmann and J. K. Taylor, *Science*, 1922 **56,** 605.

the likelihood of its occurrence, and until conclusive and infallible evidence is advanced, the case remains as heretofore—"not proven."

Further work has been carried out on the nitrogenous metabolism of the runner bean;[25] one of the active enzymes appears to be asparaginase. In *Vicia sativa*, and also possibly in *Angelica silvestris* and *Trifolium pratense*, arginase is present.[26]

In general, the later nitrates are applied to cereals, the higher is the protein content, and the greater the hardness, of the grain.[27]

It is held that in the germinating seed of *Helianthus annuus* amino-acids and proteins are oxidised with formation of ammonia, which is used by the plant in the synthesis of asparagine and glutamine.[28]

For the formation of alkaloids by the blue and yellow lupines, nitrogenous fertilisers seem to be less suitable than the nitrogenous compounds produced by the nodule bacteria, judging by the alkaloid content of plants.[29] Ciamician and Ravenna have published a summary of their work since 1908 on the biological significance of alkaloids in plants.[30]

Osmotic and Allied Phenomena.

The permeability of plant cells, the imbibition of water by plant colloids, and similar osmotic processes undoubtedly have a fundamental bearing on the phenomena of root absorption, transpiration, translocation, etc. A considerable amount of work still appears on these topics,[31] but the subject is as yet in rather a confused state, and does not lend itself to brief discussion here. Mention may, however, be made of a suggestive article by Shull[32] on osmotic

[25] A. C. Chibnall, *Biochem. J.*, 1922, **16**, 344; *A.*, i, 908; *ibid.*, 599, 608; *A.*, i, 1225.

[26] A. Kiesel, *Z. physiol. Chem.*, 1922, **118**, 254, 267; *A.*, i, 412, 413.

[27] W. F. Gericke, *Soil Sci.*, 1922, **14**, 103; *A.*, i, 1226; see also *J. Amer. Soc. Agron.*, 1922, **14**, 311; also J. Davidson, *ibid.*, 118.

[28] A. Oparin, *Biochem. Z.*, 1921, **124**, 90; *A.*, i, 309.

[29] Vogel and E. Weber, *Z. Pflanz. Düng.*, 1922, [*A*], **1**, 85; *A.*, i, 798.

[30] C. Ciamician and C. Ravenna, *Biochem. terap. sperim.*, 1922, **9**, 3; *A.*, i, 797.

[31] *Permeability* : W. J. V. Osterhout, *J. Gen. Physiol.*, 1921, **4**, 275; *A.*, i, 308; M. M. Brooks, *ibid.*, 347; *A.*, i, 308; H. Kahho, *Biochem. Z.*, 1921, **123**, 284; *A.*, i, 308; H. P. Möller, *Koll. Chem. Beihefte*, 1921, **14**, 97; *A.*, i, 95. *Imbibition :* D. T. MacDougall, *Proc. Amer. Phil. Soc.*, 1921, **60**, 15; *A.*, i, 204. *Root absorption:* G. M. Redfern, *Ann. Bot.*, 1922, **36**, 167; *A.*, i, 614; J. Stoklasa, *Biochem. Z.*, 1922, **128**, 35; *A.*, i, 502 (aluminium). *Effect of salts on plant protoplasm :* H. Kahho, *Biochem. Z.*, 1921, **117**, 87; *A.*, i, 94; *ibid.*, 1921, **120**, 125; *A.*, i, 205; *ibid.*, 1921, **122**, 39; *A.*, i, 311; W. Brenner, Hyllningsskriftillägnad Ossian Aschan, 1920, 36; *A.*, i, 907

[32] C. A. Shull, *Trans. Faraday Soc.*, 1922, **17**, 255.

phenomena in plants, and of a series of articles on permeability by Stiles.[33] The work of Priestley and his associates [34] is worthy of special mention.

Stimulant and Toxic Agents.

The favourable action of calcium salts on germination appears to be concerned with the synthetic phase of this process.[35] Lead salts exert a toxic action on the plant. They accumulate in the roots, whose growth they especially hinder.[36] The oligodynamic effect of silver is due to the silver-ion; it can be neutralised by potassium cyanide, which converts the deleterious silver-ion into the $Ag(CN)_2$-ion.[37]

It is stated that disodium arsenate has a stimulating action in low concentrations, although toxic if slightly higher concentrations are used.[38] This may, however, have been an indirect, soil effect.[39] Selenates, and particularly selenites, are markedly toxic to germination and growth of plants, as well as to *Azotobacter chroococcum*, but radium emanation is stimulating in its action on germination, and it inhibits the toxic action of selenates and selenites.[40] Sodium selenate at very low concentration is, however, stimulative to maize.[41]

Hippuric acid is toxic to plant cells at strengths above 0·09 per cent., but urea at 1 per cent. is harmless.[42] Cocaine and ecgonine are very much less toxic to *Lupinus albus* than they are to animals, but with sodium benzoate the reverse is the case.[43] From an investigation of the action of a large number of organic compounds it is concluded that, for compounds containing equal numbers of carbon atoms, the series : Amines, alcohols, aldehydes, acids, represents the order of diminishing toxicity towards plants.[44]

[33] W. Stiles, *New Phytologist*, 1922.

[34] J. H. Priestley, *ibid.*, 1922, **21**, 41, 58, 62, 113, 210, 252.

[35] L. Maquenne and E. Demoussy, *Compt. rend.*, 1922, **175**, 249; *A.*, i, 905.

[36] E. Bonnet, *ibid.*, 1922, **174**, 488; *A.*, i, 412.

[37] R. Doerr and W. Berger, *Biochem. Z.*, 1922, **131**, 151; *A.*, i, 1097; see also A. Luger, *ibid.*, 1921, **117**, 153; *A.*, i, 65.

[38] J. Stewart and E. S. Smith, *Soil Sci.*, 1922, **14**, 119; *A.*, i, 1222.

[39] See, for example, Rivière and Pichard, *loc. cit.*

[40] J. Stoklasa, *Compt. rend.*, 1922, **174**, 1075; *A.*, i, 613; *Biochem. Z.*, 1922, **130**, 604; *A.*, i, 974; B. Turina, *ibid.*, 1922, **129**, 507; *A.*, i, 707 (also tellurium).

[41] J. Stoklasa, *Compt. rend.*, 1922, **174**, 1256; *A.*, i, 614.

[42] T. Bokorny, *Biochem. Z.*, 1922, **132**, 197; *A.*, i, 1222.

[43] D. I. Macht and M. B. Livingston, *J. Gen. Physiol.*, 1922, **4**, 573; *A.*, i, 798.

[44] G. Ciamician and A. Galizzi, *Gazzetta*, 1922, **52**, i, 3; *A.*, i, 503.

The toxic action of traces of coal gas on plants is due to unsaturated hydrocarbons (ethylene), which appear to act specially in preventing normal root development.[45]

The stimulating effect of the electric discharge appears to be definitely established by field experiments on spring-sown oats and barley, but this problem is still under investigation.[46]

Plant Constituents and Products.
Inorganic Constituents.

Manganese, which appears to be an invariable constituent of plants,[47] is found in the greatest quantities in those parts of the plant such as the seeds, and young leaves where the chemical changes are most intense.[48] It has been found,[49] using many different species of plants, that in a medium entirely free from manganese growth ceases, and the plants become chlorotic, after six or eight weeks, by which time the manganese originally contained in the seed is presumably no longer sufficient. It is suggested that manganese is necessary for chlorophyll formation, and that it is concerned in nitrogen assimilation and protein synthesis, since leguminous plants are more sensitive to its absence.

Minute traces of nickel, and, with two exceptions, of cobalt, have been found in sixteen different species of common plants.[50] These two elements have also been found in minute amounts in two arable soils.[51] From the fact that the amount of nickel is much greater than that of cobalt both in the soils and in the plants examined it seems that the occurrence of these elements in the plant may be merely adventitious.

Chlorine occurs in most plants, always as chloride; it is most abundant in succulent parenchymatous tissues. Conifers, mosses, ferns, epiphytes, parasites, and saprophites contain little or no chlorine.[52] Fluorine is a normal constituent of Spanish grapes.[53]

[45] J. H. Priestley, *Ann. Appl. Biol.*, 1922, **9**, 146; see also C. Wehmer, *Bied. Zentr.*, 1921, **50**, 425; *A.*, i, 211.

[46] *J. Min. Agric.*, 1922, **29**, 792.

[47] D. H. Wester, *Biochem. Z.*, 1921, **118**, 158; *A.*, i, 94; *Pharm. Weekblad*, 1922, **59**, 51; *A.*, i, 309; G. Bode and K. Hembd, *Biochem. Z.*, 1921, **124**, 84; *A.*, i, 415.

[48] G. Bertrand and M. Rosenblatt, *Compt. rend.*, 1921, **173**, 1118; *A.*, i, 95; *ibid.*, 1922, **174**, 491; *A.*, i, 411; F. Jadin and A. Astruc, *Bull. Soc. chim.*, 1922, **31**, 917; *A.*, i, 1098.

[49] J. S. McHargue, *J. Amer. Chem. Soc.*, 1922, **44**, 1592; *A.*, i, 906.

[50] G. Bertrand and M. Mokragnatz, *Compt. rend.*, 1922, **175**, 458; *A.*, i, 1099.

[51] *Idem, ibid.*, 112; *A.*, i, 975.

[52] J. Jung, *Sitzungsber. Akad. Wiss.*, 1920, **129**, 297; *A.*, i, 1098.

[53] M. L. Pondal, *Anal. Asoc. Quím. Argentina*, 1922, **10**, 57; *A.*, i, 1100.

The amount and distribution of inorganic and organic phosphates in various seeds have been studied.[54] Marine algæ generally appear to contain a small amount of arsenic.[55]

Organic Plant Products.

Chemical work on the constitution of plant products comes within the scope of the Reports on organic chemistry, and is not considered in this Report; in this section, attention is confined to the occurrence of the different classes of organic substances in plants, and to work throwing light on the mode of formation of special classes of plant products.

Carbohydrates and Glucosides.—The sugars of wheat straw,[56] and the hemicelluloses of the seed of *Asparagus officinalis* [57] have been examined. Cytopentans is the name proposed for the "hemicellulose"-like constituents of the cell-walls of plants.[58] An improved method for the preparation of raffinose from cotton-seed meal has been described.[59] Papers have appeared on the occurrence and nature of the sugars and glucosides in *Sedum Telephium* (glucoside of an essential oil),[60] *Melampyrum arvense* (aucubin),[61] *Rhinanthus Crista-Galli* (aucubin),[62] several species of *Orchis*,[63] in the *Schrophulariaceæ*,[64] the *Caryophyllaceæ* and *Papilionaceæ*,[65] and in *Viburnum opulus*, extracts of red *Cinchona*, and the Cola nut.[66] Chinese tannin,[67] oak tannin,[68] and a crystalline tannin from *Acer ginnala* [69] have been studied. Saponins have been isolated from

[54] F. Rogozinski, *Bull. Acad. Sci. Cracovie*, 1915, [B], No. 5, 87; *A.*, i, 1226.

[55] A. J. Jones, *Pharm. J.*, 1922, **109**, 86; *A.*, i, 905.

[56] S. H. Collins and B. Thomas, *J. Agric. Sci.*, 1922, **12**, 280; S. H. Collins, *J. Soc. Chem. Ind.*, 1922, **41**, 56т; *A.*, ii, 323.

[57] W. E. Cake and H. H. Bartlett, *J. Biol. Chem.*, 1922, **51**, 93; *A.*, i, 504.

[58] D. H. F. Clayson, F. W. Norris, and S. B. Schryver, *Biochem. J.*, 1921, **15**, 643; *A.*, i, 206.

[59] E. P. Clark, *J. Amer. Chem. Soc.*, 1922, **44**, 210; *A.*, i, 323.

[60] M. Bridel, *Bull. Soc. Chim. biol.*, 1922, **4**, 242; *A.*, i, 799; *J. Pharm. chim.*, 1922, [vii], **26**, 289; *A.*, i, 1225.

[61] M. Bridel and M. Braecke, *ibid.*, 1922, **25**, 449; *A.*, i, 799; *Compt. rend.*, 1921, **173**, 1403; *A.*, i, 209.

[62] *Idem, ibid.*, 1922, **175**, 532; *A.*, i, 1225; see also *ibid.*, 640; *A.*, i, 1168.

[63] H. Hérissey and P. Delauney, *Bull. Soc. Chim. biol.*, 1921, **3**, 573; *A.*, i, 210.

[64] M. Braecke, *ibid.*, 1922, **4**, 407; *A.*, i, 1225.

[65] C. Vergelot, *ibid.*, 1921, **3**, 513; *A.*, i, 207.

[66] R. Arnold, *ibid.*, 547; *A.*, i, 311.

[67] K. Freudenberg, *Ber.*, 1922, **55**, [B], 2813; *A.*, i, 1169.

[68] K. Freudenberg and E. Vollbrecht, *ibid.*, 2420; *A.*, i, 1046.

[69] A. G. Perkin and Y. Uyeda, *T.*, 1922, **121**, 66.

Agave lechuguilla [70] and *Aralia Montana*,[71] and the effect of daylight on the content of active material in *Digitalis* has been examined.[72]

Acids and Esters.—The occurrence is recorded of citric and malic acids in *Ribes rubrum*; [73] of methyl anthranilate in grape juice; [74] of lactic acid in *Rubus idæus* (with succinic acid),[75] *R. fruticosus*,[76] *Papaver somniferum, Ricinus communis*, and *Agave Sisalana*; [77] of oxalic acid in *Acacia cambagei* (as calcium salt),[78] and in the leaves of elder, hawthorn, horse-chestnut, and barley; [79] and of malic acid in *Pyrus coronaria, Rhus glabra* (with gallic acid), *Acer saccharum*, [80] *Prunus avium*,[81] and *Pyrus aucuparia*.[82] The third optically active form of malic acid said to be present in certain plants does not exist.[83] Various esters have been identified in peaches.[84]

Triglycerides; Essential Oils.—A large number of plants and vegetable products have been examined as to their content of substances of these classes; it would, however, be neither useful nor practicable in the space available to give details here. The index of the *Journal* for 1922 should be referred to.

Pigments.—Despite the definite evidence produced by Willstätter and others, that anthocyanins are reduction products of flavones,[85] the known correlation of distribution of oxydases and of anthocyanins continues to be used as an argument for the older oxidation hypothesis.[86] It seems difficult to avoid the impression that oxidation is indeed a factor in anthocyanin formation, but it is quite

[70] C. O. Johns, L. H. Chernoff, and A. Viehoever, *J. Biol. Chem.*, 1922, **52**, 335.; *A.*, 1, 797.

[71] A. W. van der Haar, *Ber.*, 1922, **55**, [*B*], 3041; *A.*, i, 1168.

[72] O. von Dafert, *Bied. Zentr.*, 1921, **50**, 422; *A.*, 1, 97.

[73] H. Franzen and E. Schumacher, *Z. physiol. Chem.*, 1921, **115**, 9; *A.*, i, 310.

[74] F. B. Power and V. K. Chesnut, *J. Amer. Chem. Soc.*, 1921, **43**, 1741; *A.*, i, 97.

[75] H. Franzen and E. Stern, *Z. physiol. Chem.*, 1922, **121**, 195; *A.*, i, 975.

[76] H. Franzen and E. Keyssner, *ibid.*, 1921, **116**, 166; *A.*, i, 310.

[77] H. Franzen and E. Stern, *ibid.*, 1921, **115**, 270; *A.*, i, 311.

[78] T. Steel, *Chem. News*, 1921, **123**, 315; *A.*, i, 310.

[79] A. Bau, *Z. tech. Biol.*, 1921, **8**, 151; *A.*, 1, 309.

[80] C. E. Sando and H. H. Bartlett, *J. Agric. Res.*, 1921, **22**, 221; *A.*, i, 100.

[81] H. Franzen and F. Helwert, *Z. physiol. Chem.*, 1922, **122**, 46; *A.*, i, 1102.

[82] H. Franzen and R. Ostertag, *ibid.*, 1922, **119**, 150; *A.*, i, 116.

[83] *Idem, ibid.*, 1922, **122**, 263; *A.*, i, 1223.

[84] F. B. Power and V. K. Chesnut, *J. Amer. Chem. Soc.*, 1921, **43**, 1725; *A.*, i, 99.

[85] See, for example, J. Costantin, *Ann. Sci. Nat. Bot.*, 1919, [x], **1**, 38; *A.*, i, 162.

[86] M. Mirande, *Compt. rend.*, 1922, **175**, 595, 711; *A.*, i, 1224.

possible that the two views may be reconciled on the assumption that oxidation is needed in the earlier stages of the synthesis, and that only the final stage is one of reduction of flavone derivative to anthocyanin. The work of St. Jonesco [87] on anthocyanins, a feature of which is his support of the oxidation hypothesis, is held by Combes [88] to be invalidated by the fact that his (St. Jonesco's) materials are not γ-pyrone pigments but only tannins. The sap pigment of the beet root is stated to be produced by oxidation of a colourless chromogen. [89]

The presence of cyanin in the rose [90] and of pelargonin in the scarlet pelargonium [91] has been confirmed by their isolation from varieties not hitherto examined.

The colouring matters of *Lithospermum erythrorhizon*, [92] and of several species of the *Schizophyceæ* [93] have been examined. It is stated that a new class of glucosidal yellow pigments—" anthochlor "—is represented in many plants. [94]

Plant Proteins.—The chemical interpretation of differences in the quality of agricultural products is a comparatively untouched field, of great importance. A suggestive investigation [95] on the difference between the " strong " Canadian wheats and the " weak " English wheats has brought out the interesting fact that there is a difference between the glutenins of these two wheats, which is manifested by an examination of their racemisation curves. The proteins of the Adsuki bean (*Phaseolus angularis*), [96] the Lima bean (*P. lunatus*), [97] of the seed of the tomato, [98] of buckwheat, [99] lucerne, [1] *Sorghum vulgare*, [2] and of cotton seed meal, the soja bean, and the cocoa-nut [3] have been examined.

[87] St. Jonesco, *Compt. rend.*, 1921, **173**, 850, 1006; *A.*, i, 97; *ibid.*, 1922, **174**, 1635; *A.*, i, 797; *ibid.*, 1922, **175**, 592; *A.*, i, 1224.

[88] R. Combes, *ibid.*, 1921, **174**, 58; *A.*, i, 206; *ibid.*, 1922, **174**, 240; *A.*, i, 412.

[89] A. Kozlowski, *ibid.*, 1921, **173**, 855; *A.*, i, 97.

[90] G. Currey, *Proc. Roy. Soc.*, 1922, [*B*], **93**, 194; *A.*, i, 413.

[91] G. Currey, *T.*, 1922, **121**, 319.

[92] R. Majima and C. Kuroda, *Acta Phytochim.*, 1922, **1**, 43; *A.*, i, 946.

[93] K. Boresch, *Biochem. Z.*, 1921, **119**, 166; *A.*, i, 210.

[94] G. Klein, *Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 341; *A.*, i, 1099.

[95] H. E. Woodman, *J. Agric. Sci.*, 1922, **12**, 231.

[96] D. B. Jones, A. J. Finks, and C. E. F. Gersdorff, *J. Biol. Chem.*, 1922, **51**, 103; *A.*, i, 504.

[97] D. B. Jones, C. E. F. Gersdorff, C. O. Johns, and A. J. Finks, *ibid.*, 1922, **53**, 231; *A.*, i, 1101.

[98] C. O. Johns and C. E. F. Gersdorff, *ibid.*, 1922, **51**, 439; *A.*, i, 800.

[99] A. Kiesel, *Z. physiol. Chem.*, 1922, **118**, 301; *A.*, i, 412.

[1] T. B. Osborne, J. Wakeman, and C. S. Leavenworth, *J. Biol. Chem.*, 1921, **49**, 63; *A.*, i, 99; *ibid.*, 1922, **53**, 411; *A.*, i, 1104; H. G. Miller, *J. Amer. Chem. Soc.*, 1921, **43**, 2656; *A.*, i, 414.

[2] S. Visco, *Arch. Farm. sperim. Sci. aff.*, 1921, **31**, 173; *A.*, i, 211.

[3] W. G. Friedemann, *J. Biol. Chem.*, 1922, **51**, 17; *A.*, i, 505.

Plant Bases.—The alkaloid of the yew (*Taxus baccata*) has been isolated [4] and the relations between the alkaloids of the calumba root have been elucidated.[5] The alkaloid content of belladonna plants is increased by keeping them in the dark.[6] Natural muscarine has now been isolated in the pure state from *Amanita muscaria*, and it has been shown to be a base of greater complexity than choline or betainealdehyde.[7]

General.—The composition of a large number of other plants has been studied, but it is not possible to give details here. The index of the *Journal* for 1922 should be consulted.

The Chemistry of Fermentation and Enzyme Action.

It is not possible in the remaining space to deal with this subject fully. A brief survey of last year's work in this field, which makes no pretence to be exhaustive, will be given; a full discussion of the subject is reserved for a later occasion. Useful reviews of recent German work were given at the recent meeting of the Naturforscherversammlung at Leipsig.[7a]

Fermentation of Carbohydrates and Allied Substances.—Neuberg's view as to the importance of pyruvic acid in fermentation, although challenged,[8] has received further confirmation.[9] Fernbach has published a useful review of present views on the rôle of acetaldehyde.[10] Neuberg's second mode of fermentation has now been realised with various fungi [11] and with carbohydrates other than glucose.[12] Patents for the industrial preparation of glycerol by fermentation have now been published.[13] The third and fourth forms of fermentation, by which acetic and butyric acids are produced, as well as various other types of acid fermentation, have

[4] E. Winterstein and D. Iatrides, *Z. physiol. Chem.*, 1921, **117**, 240; *A.*, i, 572.

[5] E. Späth and K. Böhm, *Ber.*, 1922, **55**, [B], 2985; *A.*, i, 1174.

[6] J. Ripert, *Compt. rend.*, 1921, **173**, 928; *A.*, i, 96.

[7] H. King, *T.*, 1922. **121**, 1743.

[7a] H. von Euler, *Ber.*, 1922, **55**, [B], 3583; R. Willstätter, *ibid.*, 3601; C. Neuberg, *ibid.*, 3624.

[8] J. Kerb and K. Zeckendorf, *Biochem. Z.*, 1921, **122**, 307; *A.*, i, 305.

[9] M. von Grab, *ibid.*, 1921, **123**, 69; *A.*, i, 306.

[10] A. Fernbach and M. Schoen, *Bull. Inst. Pasteur*, 1920, **18**, 385; *A.*, i, 203.

[11] C. Neuberg and C. Cohen, *Biochem. Z.*, 1921, **122**, 204; *A.*, i, 304.

[12] M. Tomita, *ibid.*, 1921, **121**, 164; *A.*, i, 307; see also H. Kumagawa, *ibid.*, 1922, **131**, 148; *A.*, i, 972; E. Abderhalden, *Fermentforsch.*, 1921, **5**, 89, 110; *A.*, i, 92; O. Fernández and T. Garmendia, *Anal. Fís. Quím.*, 1921, **19**, 313; *A.*, i, 405.

[13] Vereinigte Chemische Werke Akt.-Ges., D.R.-P. 343321 and 347604; *A.*, i, 980.

evoked considerable research.[14] The curious action of carboligase has been further studied,[15] also the fermentation of lactic acid by yeast.[16] The stimulating [17] and toxic [18] effects of various agents on yeast fermentation and on various bacteria,[19] and moulds [20] have been studied. The claim that fermentation can be effected by mixtures containing peptone,[21] although contested,[22] appears to be justified, it being stated that dextrose is converted quantitatively by peptone at $37°$ into inactive lactic acid, using sodium bicarbonate as a buffer.[23]

The fermentation of inulin by *Monilia macedoniensis* may be used in a scheme for the identification of that carbohydrate by a mycological method.[24] In the attack of pentoses by moulds,

[14] *Acetic acid :* H. Kumagawa, *Biochem. Z.*, 1921, **123**, 225; *A.*, i, 305; E. Aubel, *Compt. rend.*, 1921, **173**, 1493; *A.*, i, 201. *Butyric acid :* C. Neuberg and B. Arinstein, *Biochem. Z.*, 1921, **117**, 269; *A.*, i, 91; M. M. Brooks, *J. Gen. Physiol.*, 1921, **4**, 177; *A.*, i, 201. *Lactic acid :* W. H. Peterson, E. B. Fred, and J. H. Anderson, *J. Biol. Chem.*, 1922, **53**, 111; *A.*, i, 971; O. R. Brunkow, W. H. Peterson, and E. B. Fred, *J. Amer. Chem. Soc.*, 1921, **43**, 2244; *A.*, i, 312 (Sauerkraut). *Silage :* A. Amos and H. E. Woodman, *J. Agric. Sci.*, 1922, **12**, 337. *Inositol fermentation :* J. A. Hewitt and D. B. Steabben, *Biochem. J.*, 1921, **15**, 665; *A.*, i, 406; H. Kumagawa, *Biochem. Z.*, 1922, **131**, 157; *A.*, i, 972. *Citromyces :* W. Butkewitsch, *ibid.* 1922, **129**, 455, 464; *A.*, i, 707; *ibid.*, 1922, **131**, 327, 338; *A.*, i, 973. *Other acids :* T. Yabuta, *J. Chem. Soc. Tokyo*, 1916, **37**, 1185, 1234; *A.*, i, 939 (*Aspergillus oryzæ*); M. Molliard, *Compt. rend.*, 1922, **174**, 881; *A.*, i, 611 (*Aspergillus niger*). *Acetone and butyl alcohol :* G. C. Robinson, *J. Biol. Chem.*, 1922, **53**, 125; *A.*, i, 971.

[15] C. Neuberg and L. Liebermann, *Biochem. Z.*, 1921, **121**, 311; *A.*, i, 305; J. Hirsch, *ibid.*, 1922, **131**, 178; *A.*, i, 973.

[16] O. Fürth and F. Lieben, *ibid.*, 1922, **128**, 144; *A.*, i, 502; *ibid.*, 1922, **132**, 165; *A.*, i, 1219; F. Lieben, *Oesterr. Chem. Ztg.*, 1922, **25**, 87; *A.*, i, 796.

[17] C. Neuberg, E. Reinfurth, and M. Sandberg, *Biochem. Z.*, 1921, **121**, 215; *A.*, i, 306; *ibid.*, 1921, **125**, 202; *A.*, i, 408; *ibid.*, 1921, **126**, 153; *A.*, i, 408; H. von Euler and S. Karlsson, *ibid.*, 1922, **130**, 550; *A.*, i, 972; P. Mayer, *ibid.*, 1922, **131**, 1; *A.*, i, 972; E. Lindberg, *ibid.*, 1922, **132**, 110; *A.*, i, 1219; T. Tholin, *Z. physiol. Chem.*, 1921, **115**, 235; *A.*, i, 305.

[18] H. Plagge, *Biochem. Z.*, 1921, **118**, 129; *A.*, i, 93; F. Boas, *ibid.*, 1921, **117**, 166; *A.*, i, 94; *ibid.*, 1922, **129**, 144; *A.*, i, 613; R. Somogyi, *ibid.*, 1921, **120**, 100; *A.*, i, 201.

[19] R. Cobet and V. van der Reis, *ibid.*, 1922, **129**, 73; *A.*, i, 611 (arsenic); L. E. Walbum, *Compt. rend. Soc. Biol.*, 1921, **85**, 619; *A.*, i, 795 (manganese); T. Duboc, *Compt. rend.*, 1922, **175**, 326; *A.*, i, 972; G. Joachimoglu, *Z. Urol.*, 1922, **16**, 97; *A.*, i, 1095; Laborde, Jaloustrc, and M. Leulier, *Bull. Soc. Chim. biol.*, 1922, **4**, 415; *A.*, i, 1219.

[20] L. Plantefol, *Compt. rend.*, 1922, **174**, 123; *A.*, i, 204.

[21] E. Baur and E. Herzfeld, *Biochem. Z.*, 1921, **117**, 96; *A.*, i, 93; *ibid.*, 1922, **131**, 382; *A.*, i, 1097.

[22] A. Bau, *ibid.*, 1921, **122**, 306; *A.*, i, 307.

[23] G. Schlatter, *ibid.*, 1922, **131**, 362; *A.*, i, 1096.

[24] A. Castellani and F. E. Taylor, *Biochem. J.*, 1922, **16**, 655; *A.*, ii, 879.

·practically the whole of the carbon consumed can be accounted for as carbon dioxide and mycelium.[25] *Aspergillus glaucus* converts glycerol into the methyl ether of a substance, $C_6H_6O_4$, which is probably a γ-pyrone derivative similar to maltol.[26] The ability of *Fusarium lini* to utilise various carbohydrates and acids has been studied,[27] also the energy yield of the growth of *Aspergillus niger* on dextrose,[28] which works out at 66—70 per cent. of that of the dextrose consumed after allowing for the maintenance requirements.

Carbohydrate-splitting Enzymes.

Willstätter is making a mass attack on the chemistry of enzymes and of enzyme action, and has published several lengthy papers on invertase,[29] raffinase,[30] maltase,[31] lactase,[32] and emulsin.[33] Although Willstätter's masterly successes in other fields of plant chemistry justify one in anticipating important results from this work, it is still in its infancy, and has not yet reached the stage when any broad generalisations emerge.

The influence of conditions on the activity of the amylases present in malt, pancreatic extract, and saliva,[34] and in *Aspergillus niger* [35] has been investigated. Euler has published several further papers on saccharase,[36] and this enzyme has also been studied by several

[25] W. H. Peterson, E. B. Fred, and E. G. Schmidt, *J. Biol. Chem.*, 1922, **54**. 19; *A.*, i, 1220.

[26] F. Traetta-Mosca and M. Preti, *Gazzetta*, 1921, **51**, ii, 269; *A.*, i, 91.

[27] Y. Tochinai, *Ann. Phytopath. Soc. Japan*, 1920, **1**, 22; *A.*, i, 207.

[28] E. E. Terroine and R. Wurmser, *Compt. rend.*, 1922, **174**, 1435; *A.*, i, 706.

[29] R. Willstätter and F. Racke, *Annalen*, 1922, **427**, 111; *A.*, i, 598; R. Willstätter, J. Graser, and R. Kuhn, *Z. physiol. Chem.*, 1922, **123**, 1; *A.*, i, 1200.

[30] R. Willstätter and R. Kuhn, *ibid*, 1922, **115**, 180; *A.*, i, 284.

[31] R. Willstätter and W. Steibelt, *ibid.*, 1921, **115**, 199; *A.*, i, 282; *ibid.*, 211; *A.*, i, 306; R. Willstätter and R. Kuhn, *ibid.*, 1921, **116**, 53; *A.*, i, 283.

[32] R. Willstätter and G. Oppenheimer, *ibid.*, 1922, **118**, 168; *A.*, i, 203.

[33] R. Willstätter and W. Csányi, *ibid.* 1921, **117**, 172; *A.*, i, 390; R. Willstätter and G. Oppenheimer, *ibid.*, 1922, **121**, 183; *A.*, i, 959.

[34] D. Maestrini, *Arch. Farm. sperim. Sci. aff.*, 1921, **32**, 40, 49, 99, **126**; *A.*, i, 507, 508; R. Lecoq, *J. Pharm. Chim.*, 1922, **25**, 18; *A.*, i, 312; F, Ducháček, *Chem. Listy*, 1922, **16**, 202; *A.*, i, 974; H. C. Sherman, *Carnegie Inst. Washington Yearbook*, 1919, **18**, 328; *A.*, i, 66; H. C. Sherman and M. Wayman, *J. Amer. Chem. Soc.*, 1921, **43**, 2454; *A.*, i, 282; H. C. Sherman and F. Walker, *ibid.*, 2461; *A.*, i, 283; U. Olsson, *Z. physiol. Chem.*, 1921, **117**, 91; *A.*, i, 300; E. Ernström, *ibid.*, 1922, **119**, 190; *A.*, i, 599.

[35] G. L. Funke, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 6; *A.*, , 796.

[36] H. v. Euler and Svanberg, *Z. physiol. Chem.*, 1921, **114**, 137; *A.*, i, 284; H. v. Euler and K. Myrbäck, *ibid.*, 1922, **120**, 61; *A.*, i, 693; H. v. Euler and D. Svanberg, *Arkiv Kem. min. Geol.*, 1922, **8**, No. 12, 1; *A.*, i, 1200; H. v. Euler and K. Myrbäck, *ibid.*, No. 17, 1; *A.*, i, 1201.

other investigators.[37]   The hydrolytic [38] and synthetic [39] actions
of emulsin have been investigated, and the isolation of active
preparations of this enzyme has been described.[40]   Emulsin is
present in a new species of yeast, *Willia javanica*.[41]   Various species
of *Rhizopus* contain a pectinase.[42]   The preparation of tannase
from a mould has been described.[43]

Saccharophosphatase has been found in the seeds of the higher
cultivated plants and in the leaves of the potato.[44]   The " in-
soluble " amylase of barley has been shown by an ingenious method [45]
to be associated with the alcohol-soluble group of proteins (hordein).

Degradation of Proteins and Amino-acids.

Papers have appeared on the degradation of proteins by yeast,[46]
on the proteolytic enzymes of malt,[47] and on the bacterial degrada-
tion of leucine,[48] tyrosine,[49] tryptophan,[50] and α-naphthylalanine.[51]

Other Enzymes.

A method for the preparation of castor bean lipase has been
described and its action studied.[52]   Lipase was also found in a

[37] W. C. Vosburgh, *J. Amer. Chem. Soc.*, 1921, **43**, 1693; *A.*, i, 64; E. W.
Miller, *J. Biol. Chem.*, 1921, **48**, 329; *A.*, i, 203; J. M. Nelson and D. I.
Hitchcock, *J. Amer. Chem. Soc.*, 1921, **43**, 1956; *A.*, i, 184; *ibid.*,
2632; *A.*, i, 388; H. Colin and A. Chaudun, *Compt. rend.*, 1922, **174**,
218; *A.*, i, 389; A. Chaudun, *J. Fabr. Sucre*, 1921, **62**, No. 39; *A.*, i, 389;
S. Kostyschev and P. Eliasberg, *Z. physiol. Chem.*, 1922, **118**, 233; *A.*, i,
410; E Canals, *Bull. Soc. chim.*, 1922, [iv] **31**, 921; *A.*, i, 1675.
[38] J. Giaja, *J. Chim. Physique*, 1921, **19**, 77; *A.*, i, 185.
[39] L. Rosenthaler, *Fermentforsch.*, 1922, **5**, 334; *A.*, i, 480; E. Nordefeldt,
Biochem. Z., 1921, **118**, 15; *A.*, i, 66.
[40] B. Helferich, *Z. physiol. Chem.*, 1921, **117**, 159; *A.*, i, 390.
[41] J. Groenewege, *Mededeel. Algemeen Proefsta. voor den Landbouw.*, 1921,
No. **9**, 1; *A.*, i, 903.
[42] L. L. Harter and J. H. Weimer, *J. Agric. Research*, 1921, **21**, 609; *A.*,
i, 507.
[43] K. Freudenberg and E. Vollbrecht, *Z. physiol. Chem.*, 1921, **116**, 277,
A., i, 285.
[44] A. Němec and F. Duchoň, *Biochem. Z.*, 1921, **119**, 73; *A.*, i, 206.
[45] J. L. Baker and H. F. E. Hulton, *T.*, 1922, **121**, 1929.
[46] N. N. Ivanov, *Biochem. Z.*, 1921, **120**, 1, 25, 62; *A.*, i, 202, 206; W.
Dieter, *Z. physiol. Chem.*, 1922, **120**, 281; *A.*, i, 795; E. Abderhalden and
E. Wertheimer, *Fermentforsch.*, 1922, **6**, 1; *A.*, i, 796.
[47] H. Lundin, *Biochem. Z.*, 1922, **131**, 193; *A.*, i, 959.
[48] M. Arai, *ibid.*, 1921, **122**, 251; *A.*, i, 303.
[49] F. Sieke, *Z. Hyg.*, 1921, **94**, 214; *A.*, i, 902.
[50] T. Sasaki and I. Otsuka, *Biochem. Z.*, 1921, **121**, 167; *A.*, i, 302.
[51] T. Sasaki and J. Kinose, *ibid.*, 171; *A.*, i, 303.
[52] D. E. Haley and J. F. Lyman, *J. Amer. Chem. Soc.*, 1921, **43**, 2664;
A., i, 390.

strain of *Aspergillus niger*.[53]. The production of fat from carbo-hydrate by the enzymes of oil seeds,[54] by yeast,[55] and by the timothy grass bacillus [56] has been investigated.

Other papers deal with the properties [57] and occurrence [58] of urease.

It is suggested that the catalase activity of seeds may be used as an indication of their germinative capacity.[59]

<div align="right">H. J. PAGE.</div>

[53] R. Schenker, *Biochem. Z.*, 1921, **120**, 164; *A.*, i, 203.

[54] L. Spiegel, *Z. physiol. Chem.*, 1922, **120**, 103; *A.*, i, 694.

[55] I. S. Maclean, *Biochem. J.*, 1922, **16**, 370; *A.*, i, 795.

[56] M. Stephenson and M. D. Whetham, *Proc. Roy. Soc*, 1922, [B], **93**, 262; *A.*, i, 500.

[57] S. Lövgren, *Biochem. Z.*, 1921, **119**, 215; *A.*, i, 185; D. H. Wester, *Pharm. Weekblad*, 1922, **59**, 173; *A.*, i, 391.

[58] A. Goris and P. Costy, *Compt. rend.*, 1922, **175**, 539; *A.*, i, 1220.

[59] A. Němec and F. Duchoň, *ibid.*, 1921, **173**, 933; *A.*, i, 94; *ibid.*, 1922, **174**, 632; *A.*, i, 411. But see J. de Vilmorin and Cazaubon, *ibid.*, 1922, **175**, 50.

CRYSTALLOGRAPHY AND MINERALOGY.

THE predominating thought which arises on commencing to write this Report, on the 27th of December in the year 1922, is that this day is the centenary of the birth of Louis Pasteur at Dôle, the picturesque little French town between Dijon and Pontarlier so familiar to travellers to Switzerland; and that the most interesting crystallographic research carried out during the year and actually communicated to the Royal Society this very month has been the elucidation by means of X-rays of the structure of the crystals of tartaric acid, and the confirmation in all essential details of the classical results of Pasteur's first research, carried out in the year 1848. The propriety of this happy coincidence, and the completeness of the proof of the accuracy of this crystallographic work of Pasteur, will, indeed, go down to posterity as one of the most romantic events in the history of the science. It reminds us very forcibly that the great French savant was a skilled crystallographer first, and a benefactor of the human race by his wonderful bacteriological successes afterwards.

Molecules in the Crystalline Condition.

In last year's Report the writer uttered a protest against the very premature statements which had been made by certain authors, shortly after the announcement of the first results of X-ray analyses of simple binary compounds and elementary substances, that chemical molecules do not exist in the crystalline condition. The writer's own researches had indicated exactly the contrary, and that in most cases of chemical compounds the crystal unit, the similar repetition of which built up the crystal and the representative point of which formed by its repetition in space the space-lattice, was composed of two to four or other small number of chemical molecules; and that within this polymolecular crystal unit, the grosser unit of the crystal structure and the unit cell of the space-lattice, the two, four, or other small number of molecules were mutually arranged in such a manner that the atoms composing them were situated so as to make up one of the 230 types of homogeneous structure which alone are possible to crystals. Although in very simple cases such as those of rocksalt, NaCl, and zinc blende, ZnS, the type of structure is so very simple that molecules may not be

definitely identifiable, they are there all the same, for they enter as such from the mother-liquor on crystallisation, and they are again recoverable on solution in a solvent or on fusion to the liquid state. In more complicated cases of substances composed of many atoms it was inconceivable that the molecules were destroyed, on entering the crystal to assist in building up the solid edifice.

The important work of Sir William Bragg on the structure of naphthalene and its derivatives and anthracene, the results of the X-ray analysis of which were fully described in the last Report, gave the first experimental X-ray evidence of the truth of the writer's views as above expressed. For it was conclusively proved that the chemical molecules of these many-atomed organic substances entered into the crystals intact, that the crystal-units of naphthalene and anthracene are each composed of two molecules, and that those of acenaphthene, α-naphthol, and β-naphthol each contain four molecules.

It was further shown that when a crystal forms in a liquid, or by ˙sublimation, each molecule which takes part in forming the crystal is fixed by the attachment of certain very definite points on its own structure to certain equally specific points on the structure of another molecule, the precision of the adjustment being beautifully exact, indicating very definite form on the part of the molecule, and that the forces exerted have very short ranges. In the case of naphthalene, for instance, the molecules arrange themselves alongside each other, and so that the α-hydrogens of each molecule seek to attach themselves to the carbon atoms of the neighbouring molecules. The two molecules thus enter the crystal unit in each case intact, and the similar repetition of this polymolecular unit, as the unit cells of a particular space-lattice, forms the crystal. For the molecules become locked into the crystal structure when attachments are made at sufficient points, the whole structure being then as definite and stable as the most perfect engineering structure.

Further work during the year 1922 has united in offering additional confirmation of these now indisputable facts, and it was admirably summarised, and new results referred to, in the lecture which was delivered to the Chemical Society on October 26th by Sir William Bragg.[1] Moreover, a definite law has been advanced by one of his collaborators, Mr. G. Shearer,[2] as expressing the results of investigations carried out at University College, London, to which further reference will be made later in this Report.

Sir William Bragg began his lecture with the recognition of the fact that " every crystal is built up by the repetition throughout

[1] Sir W. H. Bragg, *T.*, 1922, **121**, 2766.
[2] G. Shearer, *Proc. Physical Soc.*, 1922.

its volume of a certain unit," that " the repetition is exact in every detail, so that each unit is a perfect epitome of the whole." In fact he adopts as correct the statement of Barlow [3] that " a homogeneous structure is one, every point within which, if we regard the structure as without boundaries, has corresponding to it an infinitude of other points whose situations in the structure are precisely similar." Having adopted the conception of the unit cell, Sir William agrees to call it the " crystal unit." R. W. G. Wyckoff [4] has come to a somewhat similar conclusion, but has, unfortunately, given the name " crystal molecule " to this unit polymolecular cell, which is to be deprecated as confusing, for crystal molecule is better left to express a chemical molecule as found in the crystal. Sir William then showed that there is no reason to suppose that, in general, the crystal unit is the chemical molecule, but that there is every reason to expect the contrary. The properties of the molecule are those of the substance in the liquid or gaseous state, whereas the solid substance possesses a large number of properties which the liquid substance does not possess. There may be cases where the molecule is the crystal unit (some will be subsequently referred to), but in general this is not so, and Sir William instanced silicon dioxide, SiO_2, the chemical molecule of which is incapable, by itself, of producing the rotation of the plane of polarisation of light, which is so characteristic a property of quartz, the crystallised dioxide, which X-ray analysis has shown to consist of crystal units made up each of the substance of three molecules of SiO_2.

Further, it does not follow that the molecule exists in the crystal in exactly the same form and condition as in the liquid or gas; the disposition of the constituent atoms may be different (strained or distorted), although in most cases the difference is but slight and certainly not constitutional. For instance, in naphthalene each of the two molecules $C_{10}H_8$ probably resembles very closely in shape the molecule in the liquid state. Still further, X-ray analysis has shown clearly that the crystal unit nearly always contains the substance of more than one molecule, usually two, three, or four. It has also very clearly indicated that the atoms in the unit can be divided into groups, each containing the substance of one molecule.

In the case of organic crystals it has proved to be a very clear division into molecules. But in such simple cases as rocksalt and diamond it is very faint or even indistinguishable. For instance,

[3] W. Barlow, *Min. Mag.*, 1895, **11**, 119.

[4] R. W. G. Wyckoff, " The Analytical Expression of the Results of the Theory of Space-Groups," Carnegie Inst. Washington, Publ. No. 318, p. 43.

the four molecules of NaCl constituting the crystal unit of rocksalt have apparently become indistinguishable. Yet there are some indications "of association of a sodium atom at the edge of the cube with a chlorine atom lying along the digonal axis through the sodium. Indeed, in sylvine, KCl, this trace of association is sufficient to affect the form of the crystal, giving it the drop in symmetry which it actually shows" (Sir William Bragg in a communication to the writer just received).

With every word of the above, crystallographers can heartily agree, and will be grateful to Sir William Bragg for having so thoroughly cleared the air, and removed the gross misconception which had arisen, according to which crystals were to be regarded in all cases as merely assemblages of "ions," which were confused with those of the electrolytic dissociation hypothesis.

The sense in which "ionisation" is to be understood in connexion with crystal structure was explained in the last Report (pages 220 and 221). It relates only to that one of the two types of chemical combination which is characterised by "electrovalency" (Langmuir), the transference of an electron or electrons from an electropositive atom, having an excess for inert gas stability, to an electronegative atom deficient in electrons. The other type of combination is characterised by "co-valency," electrons being shared by two electronegative atoms to make up their common deficiency; the atoms are bound more closely together by this co-valent type of combination. Even in the case of electrovalent combination, however, where it is due to electrostatic attraction owing to the two atoms being left oppositely electrified by the transfer, it has been shown that evidence has been found by Sir William Bragg, notably in the case of potassium chloride, that the molecules formed retain their identity in the crystal structure. In the case of co-valency combination, the molecules are obviously very clearly identifiable.

Sir William recalled that the form of the crystal unit is precisely defined in absolute measure by X-ray analysis, and is necessarily a parallelepiped, the unit cell of the space-lattice, bounded by three pairs of parallel faces, the distance between a pair, now known as the "spacing" of the plane parallel to the pair, being determined by the now famous expression : $\lambda = 2d \cdot \sin \theta$, where λ is the wavelength of the X-rays used, d is the spacing, and θ is the smallest of the glancing angles which the incident X-rays must make with the plane in order that reflection may occur. When the spacing of the three pairs of cell-faces is determined, the volume of the unit cell can, of course, at once be calculated. Moreover, the weight of the cell contents is found by multiplying by the density, and the

number of molecules in the unit cell is found by dividing this weight by the weight of the molecule.

The shape of the unit has infinite possibilities, for the corners are all alike in Barlow's sense, that from each of them the outlook is the same; it is these corners, with all the similar points throughout the crystal, which make up the space-lattice. It comes to the same thing as regarding the centres of the cells (or any other identically chosen representative point) as the points of the space-lattice.

A wide field of research now opens out, the determination of the physical constants of this polymolecular crystal unit, inasmuch as it possesses all the properties of the crystal. Its elastic, electric, optical, and thermal, indeed all vectorial, properties and constants now become of immense importance, and all of them will be intimately connected with the detailed internal structure of the crystal unit, that is, with the positions of the atoms composing it, and not improbably with the distribution of the electrons on the atoms. This detailed structure we can look to X-ray analysis to afford. us. It has to be remembered, however, that X-rays cannot distinguish between the two sides of a set of reflecting planes. For instance, in zinc blende the two ends of the polar crystal cannot be discriminated, although the distance between the alternating planes, say those parallel to (111), of zinc and sulphur is three times as great going from zinc to sulphur one way as it is when going the other way. For the intensities of the different orders of X-ray spectra reflected depend on the relative magnitude of the spacings and not on their order. Similarly, X-rays cannot discriminate between a right-handed spiral and a left-handed one, for the one is the reflection of the other.

The number of chemical molecules in the cell (crystal unit) turns out to be intimately connected both with the symmetry of the crystal and with that of the molecule. For instance, while naphthalene has two molecules in the crystal unit, α-naphthol, in which a hydroxyl group is substituted for one of the hydrogen atoms of naphthalene and which must therefore be less symmetrical, has four molecules to the crystal unit, the symmetry remaining monoclinic prismatic (holohedral). Similarly, while two molecules of benzene go to the crystal unit of benzene, four molecules are present in the crystal unit of benzoic acid, the molecule of which is obviously more unsymmetrical, and in this case the symmetry is also lower. The symmetry of the crystal thus increases with the number of molecules in the crystal unit, and also with the symmetry of the molecule itself.

The paper of Mr. G. Shearer,[2] already mentioned, was read to the

[2] G. Shearer, *Proc. Physical Soc.*, 1922.

Physical Society on December. 8th, 1922, and the writer is able to give some account of it, as he has been most kindly permitted to see the proof-sheets. It discusses very fully the number of asymmetric molecules necessary *per* crystal unit to produce the symmetry of the 32 classes of crystals. The existence of fewer than this number of molecules in the crystal unit is shown to imply symmetry in the molecule itself. The relative positions of the variously orientated molecules in the lattice are also considered, and it is shown that only certain positions are possible. Further, it is concluded that the number of molecules in the elementary cell of the space-lattice is always the minimum necessary to satisfy the symmetry conditions, and that any symmetry of the molecule is reproduced in the crystal. Hence, the crystal always shows at least as much symmetry as the molecules which form it; indeed, in general, the symmetry of the crystal is higher than that of the molecule. Shearer's conclusions are then embodied in the following two rules : (1) The number obtained by dividing the weight of the crystal unit by the molecular weight is either equal to the symmetry number (the number of asymmetric molecules in the unit) or is a sub-multiple of it. (2) In the latter case, the number obtained by dividing the symmetry number by the number of molecule sis the symmetry number of the molecule.

Shearer's first rule emphasises the fact that the chemical molecule is the basis of construction of the crystal unit, and thus lays still further stress on the persistence of the molecule in the solid crystal-line condition. No case has yet been observed in which the number of molecules is greater than the symmetry number, but cases where it is smaller are common. For instance, the great majority of organic substances examined by X-rays crystallise in the prismatic (holohedral) class of the monoclinic system, their symmetry number is four, and four molecules are found in the crystal unit cell. This obviously corresponds to molecules having no symmetry, which is very general for organic compounds.

The work of Sir William Bragg and his collaborators has shown conclusively that it is possible to obtain decisive evidence of the position of the individual molecules in a polymolecular crystal unit, and also of the positions of the various atoms making up each molecule.

Taking this in conjunction with the rules of Shearer, it is now further possible to obtain a clue to the symmetry of the mole-cule itself. Sir William has laid down two definite principles concerning the positions of the molecules in the unit. (*a*) If a crystal unit contain two molecules, one of which is the reflection of the other across a plane of symmetry, and each corner of the unit be occupied by a representative of one of the two types of

molecule, then the molecule of the other type must lie on a line perpendicular to the plane of reflection, and passing through the centre of one of the cell faces. (*b*) If a crystal unit contain two molecules, one of which can be brought to coincidence with the other by a digonal axial rotation (the crystal then possessing a plane of symmetry perpendicular to the axis), and if the crystal unit be so placed that each of its corners is occupied by one of the two types of molecule, then the molecules of the other type must lie on planes perpendicular to the axis and passing through a face-centre.

Now the "spacing" is the distance between any plane and the nearest parallel plane which is identical with the former as regards its relation to the crystal structure. And if there are four molecules in the unit, all four are, in general, differently related to any plane in the crystal. If, for example, the digonal molecules of case (*b*) lie in planes interleaving the planes of the other molecules, the spacing is halved (that of (010) for instance); this occurs in naphthalene and benzoic acid. If, on the other hand, the digonal molecules lie in the same planes as the original molecules, the spacing is not altered, and this occurs in the two naphthols. Thus by the halving or otherwise of the spacing the positions of the constituent molecules of a crystal unit can be clearly ascertained. For instance, the positions of the four molecules *A*, *B*, *C*, *D*, of benzoic acid, $C_6H_5 \cdot CO_2H$, are shown in Fig. 1. The spacings were determinable with great accuracy, as very strong reflections of the X-rays were obtained. The presence of double layers parallel to the (001) plane, and parallel to the very perfect cleavage, is also clearly shown, and the flakiness of benzoic acid crystals is explained by

FIG: 1.

$Oa = 5 \cdot 44; \; Ob = 5 \cdot 18; \; Oc = 21 \cdot 6;$
$\beta = 97° 5'.$

Crystal Unit Cell of Benzoic Acid.

the much closer packing of the molecules along this plane than the other principal planes.

As regards the kind of conclusions to be drawn concerning the symmetry of the molecule itself, when the number of molecules in the crystal unit is less than the symmetry number, the case of naphthalene may again be considered as an example. The symmetry number is four, but there are only two molecules to the crystal unit; hence, the symmetry number of the molecule is two, that is, it possesses twofold symmetry and no more. This is strictly demonstrable only for the crystal molecule (the chemical molecule as it exists in the crystal), yet there must be some character in the substance which disposes its molecule $C_{10}H_8$ to take up one or other of the two mutually digonal forms according to the circumstances in which it finds itself. Moreover, the X-ray results prove that the molecule of naphthalene must have either a plane of symmetry,

<table>
<tr><td>FIG. 2.</td><td>FIG. 3.</td></tr>
</table>
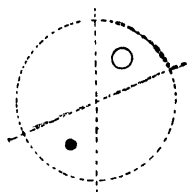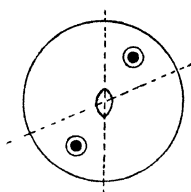
<table>
<tr><td>The Molecule.</td><td>The Crystal Unit.</td></tr>
</table>

The Symmetry of Naphthalene.

a centre of symmetry, or a digonal axis. The evidence at the time of Sir William's lecture was insufficient to decide which of the three alternatives is correct, but the balance of evidence favoured the centre of symmetry, the B molecule being both the reflection and the digonal complement of the A molecule, as illustrated by Figs. 2 and 3, the former representing the symmetry of the molecule and the latter that of the crystal unit (monoclinic prismatic).

In the private communication to the writer already referred to, Sir William states that he has cleared up the doubt, and that the spacing thought at first to be a full one is really halved, and that there is no doubt whatever that the crystal molecule of naphthalene has a centre of symmetry.

In this letter to the writer Sir William Bragg also makes a further statement regarding anthracene, which is important as it opens up a new method, by use of X-rays, of determining the density of crystallised substances. He has redetermined the spacings with some excellent little crystals provided by Dr. Brady, and these

much more accurate measurements show that the c-axis is exactly 2·5 longer than in the case of naphthalene, just the right amount to correspond to an extra ring. The new numbers are: $a = 8.58$; $b = 6.02$; $c = 11.18$; $\beta = 125° 0'$.

The b-axis of naphthalene was found to be 5·98, practically identical with that of anthracene. On working out the density of anthracene from this new information it is found to be 1·255, and this is probably much nearer the truth than the very approximate value, 1·15, given in physical tables. Sir William considers that as the X-ray methods give the actual (absolute) dimensions of the crystal structure they afford a means of determining the density free from errors of inclusions of various sorts.

Some additional X-ray data concerning benzene itself were given in his lecture by Sir William Bragg. The symmetry number of the

FIG. 4.
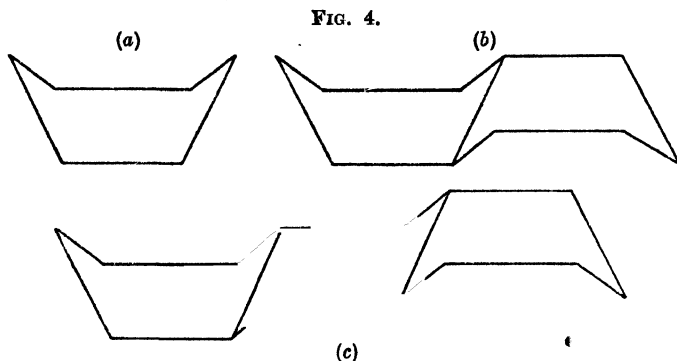
Diagrammatic Forms of (a) Benzene, (b) Naphthalene, (c) Anthracene Molecules.

crystal is eight, as it belongs to the rhombic bipyramidal (holohedral) class, but there are only two molecules contained in the crystal unit. Each molecule possesses, therefore, fourfold symmetry. But it has neither a trigonal nor a hexagonal axis, and therefore the conventional method of representing the molecule as a hexagon is not in accordance with fact. The correct arrangement is slightly different from the sixfold arrangement of carbon atoms in the dia-mond, and it is shown in perspective in Fig. 4, which also shows at (b) the arrangement in naphthalene and at (c) that in anthracene. The figure of benzene at (a) has the correct amount of symmetry for the molecule of benzene as it occurs in the crystal; it is more in accordance with the Dewar or Ladenburg formula than with that of Kekulé or of Claus. It will be remembered that the formula of Dewar is that here shown, the suffix after the C representing the order of the carbon atom and not the number of atoms. .

$$\begin{array}{c} H \\ C_5 \\ HC_6 \diagup \alpha \diagdown C_4H \\ \beta \quad \beta \\ HC_1 \diagdown \beta \diagup C_3H \\ \alpha \quad \alpha \\ C_2 \\ H \end{array}$$
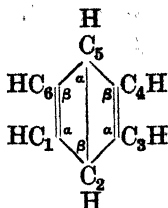
It probably possesses a plane of symmetry and an axis of symmetry perpendicular to it, but this is not trigonal. The figure for the two-ringed molecule of naphthalene at (*b*) has a centre of symmetry only, which has just been shown to be the fact. That at (*c*) for anthracene has a third ring of the diamond form inserted between

FIG. 5.
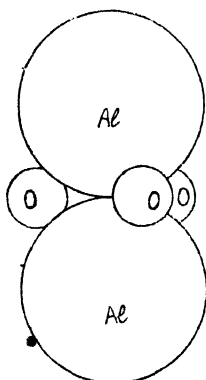
The Crystal Molecule of Al_2O_3, showing arrangement of Atoms.

FIG. 6.
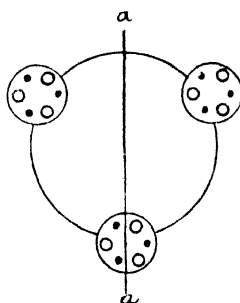
Section through Centre of Molecule, showing arrangement of Electrons in the Oxygen Atoms.

those of naphthalene. The sides of all the hexagons are equal, but do not lie in a plane, and the angle between any pair of adjacent sides is the tetrahedral angle 109° 28′.

As a couple of final examples of the truth of Shearer's rules, the simpler inorganic cases of quartz and corundum may be referred to. The quartz crystal is of sixfold symmetry, and as its crystal unit contains three molecules of SiO_2, spirally arranged in accordance with trigonal (class 18) symmetry, each molecule has twofold symmetry only. The crystal possesses digonal axes, hence the molecule of SiO_2 has digonal symmetry. Corundum has twelvefold (trigonal class 21) symmetry, with a crystal unit comprising two molecules of Al_2O_3, the axial ratio being $a : c = 1 : 2·73$ and not $1 : 1·365$ as usually given. The molecule, therefore, possesses sixfold sym-

metry.   X-Ray determinations with the ruby indicate the structure shown in Fig. 5, which agrees with trigonal symmetry, but does not show the nature of the additional twofold symmetry.   In Fig. 6, which shows a section of the molecule, the digonal axis is, however, clearly visible at *aa*.   Thus the molecule contributes the trigonal and digonal axes, while the crystal structure contributes the planes of symmetry which are characteristic of class 21, for the molecule itself has no plane of symmetry.   Sir William Bragg and Mr. Shearer both suggest that, as indicated in Fig. 6, the distribution of the six electrons in the outer shell of the oxygen atoms is such as determines that the crystal shall have the three symmetry planes, in addition to the symmetry elements already present in the molecule owing to the positions of the atoms.

There has thus been accumulated a mass of evidence that the rules enunciated by Shearer are truly valid.   The case of tartaric acid is another contributing weighty evidence in the same direction, but this is an altogether remarkable and exceptionally interesting case and will be dealt with in a separate section.   Before passing to this, however, reference may be made to an important question raised by Shearer : What determines the choice by any substance of the peculiar form characteristic of itself ?   For if the molecule be asymmetric all the 32 classes are open to it to crystallise in. But it is very improbable that it will choose the class 32 of highest cubic symmetry, for 48 molecules would then be required to form the crystal unit, whereas 8 molecules is about the maximum number yet found in any space-lattice cell, and this is very exceptional. Asymmetric molecules will therefore crystallise in classes of low symmetry, which is, indeed, found to be the case.   Out of a thousand organic aromatic compounds passed in review 60 per cent. require only four molecules to the crystal unit.   If, however, the molecule possess some symmetry, its choice will fall on a higher class of symmetry, the higher the greater the symmetry of the molecule.

The Structure of Tartaric Acid.

The coincidence is a most happy one, that the structure of tartaric acid has been successfully determined by Mr. W. T. Astbury,[5] in Sir William Bragg's laboratory, at the very time of the Pasteur centenary.

In the paper read to the Royal Society on December 7th, 1922, presenting the results of the X-ray spectrometric analysis, not only are the conclusions of Pasteur confirmed in absolute measure, but some of the more obscure of the properties of this exceptionally interesting and important substance are cleared up by the nature of

[5] *Proc. Roy. Soc.*, 1922, [A].

the structure which is revealed. The crystal structure of ordinary tartaric acid proves to exhibit just such a spiral arrangement of the four carbon atoms of the molecule as was assumed from the crystallographic, enantiomorphous, character of the crystals and from their dextrorotatory power. The theory of stereoisomerism of Le Bel and van't Hoff is in its essentials confirmed, and the direct link between the crystallographic enantiomorphs and the chemical stereoisomerides is revealed. But it is shown to be impossible to distinguish between the dextro- and lævo-forms of such an optically active enantiomorphous substance. The structure established, however, affords a simple explanation of the anomalous rotatory dispersion, involving a maximum for a specific wave-length of light, which is exhibited both by tartaric acid and by its derivatives.

The Bragg ionisation-spectrometer and a Coolidge bulb with molybdenum anticathode were employed, the crystals used being

FIG. 7.　　　　　　　　　　　FIG. 8.
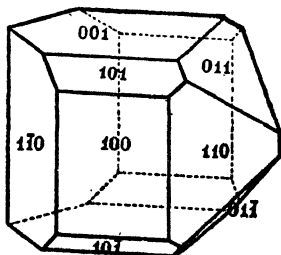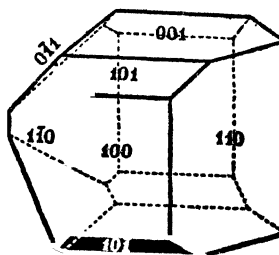
dextro-Tartaric Acid.　　　　　lævo-Tartaric Acid.

those of ordinary (dextro) tartaric acid, $C_4H_6O_6$. The crystals belong to the sphenoidal class 4 of the monoclinic system, and their constants are $a : b : c = 1\cdot2747 : 1 : 1\cdot0266$; $\beta = 100°\ 17'$; density $1\cdot759$. The next two figures (Figs. 7 and 8) represent two typical crystals of the dextro- and lævo-varieties of tartaric acid, which differ essentially by the dextro-crystal exhibiting only the right clino-prism {011} and the lævo-crystal only the left clino-prism {0$\bar{1}$1}.

The crystal unit is found to contain two molecules $C_4H_6O_6$, and as the symmetry number is two, each molecule must be asymmetric in accordance with Shearer's rule, and with the absolutely essential condition for optical activity, the absence of second-order symmetry elements, symmetry planes being certainly absent. The crystal also being likewise optically active, must be without any plane of symmetry, and must possess some kind of spiral structure, which is right-handed in one of the active varieties and left-handed in the other.

The structure which Mr. Astbury eventually deduces from his

X-ray spectrometric measurements of spacings and intensities of the various spectral orders, together with the known crystallographic and density data above given, is shown in Fig. 9. The portion of the figure marked I shows the crystal unit of tartaric acid and the arrangement of the molecules. Of the two molecules forming each crystal unit one is the digonal complement of the other, and the spacing of the (010) planes is found to be halved in consequence. Moreover, the structure exhibits not only one spiral but two spirals, differently handed but not mirror-image complements and occurring in different parts of the structure. One is associated with the four carbon atoms at the centre of the molecule

Fig. 9.

— TARTARIC ACID.— CH(OH)·COOH·COOH CH(OH). —
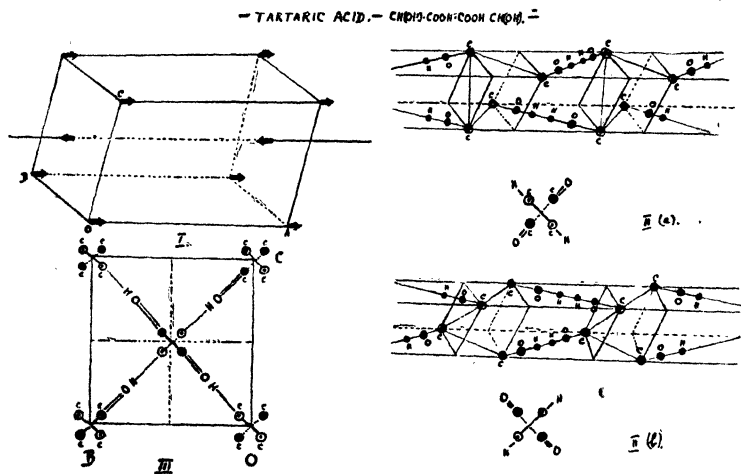
The Structure of Tartaric Acid.

and forming its nucleus, and the other with the four hydroxyl groups. To the former spiral is due the optical activity of the solution, for it is permanent, persisting in the molecule itself; whereas the latter spiral appears only in the crystal structure and disappears in solution. Its rotation effect on the plane of polarisation of light is greater than that in the opposite direction due to the first screw, and so determines the sign of rotation of the tartaric acid crystal, which appears to be the opposite of that of the solution.

Parts II(a) and II(b) show the two enantiomorphous forms of the crystal unit, and the arrangement of the two molecules along the axis a, as well as the projection of the carbon core on a plane perpendicular to axis a. Part III shows the section of the crystal unit perpendicular to axis a, with the arrangement of the molecule

at each corner and its digonal complementary molecule at the centre.

This structure agrees with all the purely crystallographic data concerning tartaric acid. The two forms shown at II(a) and II(b) are clearly enantiomorphous with respect to each other. It also explains the one perfect cleavage parallel (100), the plane about which lie the junctions of the hydroxyl groups. For the molecules are held together end to end by forces between the hydrogen atoms of adjacent hydroxyl groups, one OH group being carboxylic and the other alcoholic. None of the strong valency forces acts across this plane (100), but only these weaker forces acting from molecule to molecule and serving to bind them together in the crystal lattice; hence, it is pre-eminently a plane of possible cleavage, as is actually observed. The junctions in the (=OH-) linkages are stronger, hence, there is no cleavage across them, doubtless due to the oxygen having double linkage. The distance between carbon and oxygen atoms in the (-C=O) groups is also less than in the (-C-O-H) groups, and this is doubtless due to electron-sharing.

Another interesting fact is that there is a particularly intense first-order reflection of the X-rays from the (011) plane, and it is precisely this plane which has the greatest density of atoms per unit area; the interleaving also throws most of the energy into the first-order spectrum from this plane. Now the crystals themselves usually develop these planes characteristically, (011) on right-handed crystals and (0$\bar{1}$1) on left-handed ones, as shown in Figs. 7 and 8. This agrees with the well-known crystallographic principle that a crystal tends to develop best the planes of greatest reticular density.

The spiral nature of the two enantiomorphous structures shown at II(a) and II(b) will be obvious, and the fact that they are of opposite winding. The four carbon atoms which form the nucleus of the molecule are situated at alternate corners of the oblique parallelepiped, and this automatically produces an irregular spiral formation within the molecule itself. Moreover, the hydroxyl groups are arranged in another spiral of opposite kind, the junction between the hydrogen atoms being only possible when this is so, this second twist reversing, and more, the twist of the nucleus of the molecule just described. Each of these twists in one enantio-morph is the opposite of that in the other, and this reversal of twist inverts the order of succession of the (-H), (-OH), and (-CO·OH) groups round the asymmetric carbon atoms.

The structure agrees with the fact that the plane of the optic axes of tartaric acid is perpendicular to the one symmetry plane of the monoclinic crystal, the obtuse bisectrix coinciding with the

unique digonal symmetry axis b, so that the two optic axes make equal angles with axis b; it consequently also agrees with the fact that the rotatory power along each of the two optic axes is the same, namely, according to Dufet 8° 33′ per millimetre of thickness of plate for red lithium light, increasing with shortening wave-length to 14° 14′ for green thallium light.

The unusual property was discovered by Biot, that solutions of tartaric acid in water or alcohol show a maximum rotation in the green, and also that the specific rotation of an aqueous solution at a given temperature is a linear function of the concentration: $[\alpha] = A + B\epsilon$, where ϵ is the proportion of water in the solution. By extrapolation he also obtained the rotation of the anhydrous acid, and predicted that for red light this would change sign at 23°. This prediction was subsequently verified. Now these remarkable facts are also explained by the structure of the crystals as now revealed by X-rays, the two opposite rotatory systems produced by the two opposite spiral twists of the two parts of each molecule being adequate to account for them completely. The involved explanation suggested by Lowry is thus unnecessary, the structure alone affording a sufficient cause.

The final conclusion is that the dextrorotatory power of ordinary tartaric acid is to be ascribed solely to the presence within the molecule of a system of four carbon atoms forming an irregular spiral. The direction of twist of this spiral is the opposite of what it is in *lævo*-tartaric acid. Arguing from the analogy of Reusch's pile of mica plates simulating quartz and its rotation, a clockwise spiral of atoms will produce dextrorotation (meaning that the plane of polarisation of light is rotated to the right or to the left from the point of view of a person looking into the microscope), and an anti-clockwise spiral lævorotation. In *dextro*-tartaric acid the order of sequence of the (–H), (–OH), and (–CO·OH) groups is anti-clockwise, as we look towards the asymmetric carbon atom in the direction leading towards it from its companion asymmetric carbon atom. The aspect of the molecule as a whole shows a distorted tetrahedral arrangement of bonds.

It would thus appear that the structure arrived at as the result of this interesting investigation explains in a most satisfactory fashion even the smallest details of the physical properties, in many ways peculiar and unusual, of tartaric acid, as well as confirming the general conclusions of Pasteur and later workers as to the essential characters of the two varieties and their relations to the optical activity of this typical enantiomorphous substance, the first of the large class of such substances which have since become known.

Further Light on Functions of Exterior Electrons.

It was shown in the last Report that some light had been thrown on the situation of the outer electrons of the atoms by some special experiments, concerning the intensity of certain orders of X-ray reflection from the planes of atoms in the diamond and fluorspar, by Sir W. H. Bragg and Mr. H. Pealing. It is immaterial, as regards the symmetry of the atoms, whether the electrons are stationary or moving in orbits, so long as in the latter case the distribution of the orbits or of their normals is considered. In any case, the outer electrons are prime factors in the problem of atomic symmetry, and the concluding portion of Shearer's paper [2] deals with this aspect of the subject. Now a considerable number of the elements crystallise in the highest class 32 of cubic symmetry, while the crystal unit only contains two or four atoms.

If we consult Shearer's table giving the number of asymmetric molecules required to build up the crystal unit in each of the 32 classes (this number varies from 1 in class 1 to 48 in class 32), and divide the 48 there given as corresponding to class 32 by 2 or 4, we arrive at 24-fold or 12-fold symmetry as being that possessed by these elementary atoms, and this corresponds to one of the lower classes of the cubic system. From this Shearer concludes that there is some form of cubic arrangement of the electrons or their orbits in these atoms. Carbon, in the diamond form, even if considered as only belonging to class 31 (whereas there is more evidence that it really belongs to class 32), as it has eight atoms to the crystal unit, would have the symmetry number three, and would therefore possess a trigonal axis. Hull's structure for graphite also supports the assumption that the carbon atom possesses a trigonal axis of symmetry in its structure. It would thus appear that for crystallographic purposes what matters is the outer electronic arrangement, and not the atomic nucleus.

In the last Report it was also shown that a formula for the intensity of reflection from a crystal plane of atoms had been arrived at by W. L. Bragg, R. W. James, and C. H. Bosanquet, embodying also some important results of C. G. Darwin and A. H. Compton, and also those of P. Debye and P. Scherrer, in which occurred an important factor, F, which depended on the number and arrangement of the electrons of the diffracting atoms constituting the plane. C. G. Darwin,[6] however, has since shown that on account of the difficulty in determining the effective coefficient of extinction of the X-rays the result afforded by the formula is not quite accurate, and has suggested a new formula, based on his experiments with powdered crystals, as affording more accurately the

[6] C. G. Darwin, *Phil. Mag.*, 1922, [vi], 43, 800; *A.*, ii, 416.

amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam. A. H. Compton and N. L. Freeman [7] have also arrived at the same conclusion, and have made quantitative measurements of the intensity of X-rays derived by reflection from rocksalt and then scattered by powdered crystals of sodium chloride, using the K_a line from molybdenum ($\lambda = 0\cdot708$ Å.U.). They found that the theory of X-ray reflection which has been put forward by Sir W. H. Bragg then gives accurate results. In a further paper, W. L. Bragg, James, and Bosanquet [8] revise their results in the light of these contemporary researches, and have reduced the error due to the extinction uncertainty to a minimum. The results then indicate that neither in the sodium nor the chlorine atom can there be eight electrons in an outer shell, or eight electrons describing orbits lying on an outer sphere; but that a combination of circular and ellipitic orbits would agree with the F curves as now corrected. This would appear to indicate that the theories of Bohr and of Langmuir concerning atomic structure are neither alone correct, and that the truth lies somewhere between the two, a conclusion which has lately been emphasised from all sides.

Effect of Temperature on X-Ray Reflection.

This has been studied during the year by I. Backhurst [9] in Sir W. H. Bragg's laboratory. According to C. G. Darwin and to P. Debye the intensity diminishes as the temperature of the crystal increases, and it does so more rapidly as the angle of reflection increases. These conclusions were supported by experiments made some time ago by Sir William Bragg, and are now fully confirmed by Mr. Backhurst's results.[9] Sir W. H. Bragg's apparatus was used, the crystal being placed in an electric heater furnished with mica windows for ingress and egress of the X-rays, the thermometer bulb being immediately over the crystal. Sir W. H. Bragg's original apparatus only permitted of determinations with rocksalt and sylvine up to 370° and 311°, respectively, but in the new arrangement a much higher temperature can be maintained, and the crystal be environed by an atmosphere of nitrogen, a thermocouple being substituted for the thermometer at the higher temperatures. Crystals of aluminium, carborundum, graphite, diamond, sapphire, and ruby were studied. Aluminium showed a very marked decrease of reflection intensity with rise of temperature, in fair agreement with Debye's theory. Carborundum proved stable enough to be tested (using a special furnace) up to as high a tempera-

[7] A. H. Compton and N. L. Freeman, *Nature*, 1922, **110**, 38.

[8] W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.*, 1922, [vi], **44**. 433: *A.*, ii, 703.

[9] I. Backhurst, *Proc. Roy. Soc.*, 1922, [*A*], **102**, 340.

ture as 960°, and gave much greater decreases of intensity for the higher spectral orders. Graphite, studied up to 850°, agreed with theory, but also showed an unusually high coefficient of expansion perpendicular to (0001), which further emphasises the weakness of the bonds in this direction referred to in the last report. Diamond was remarkable as showing practically no decrease of intensity, owing to its great strength and the slight degree of thermal agitation which it evinces. Ruby and sapphire showed an anomalous effect, indicating that the pair of aluminium atoms remain in contact and do not share in the expansion of the lattice which is observed.

Crystal Structure as determined by X-Rays and the 230 Space-groups.

A fact which has become more and more emphasised during the year is that all the results of X-ray analysis of crystals which are open to no ambiguity have shown that the crystal structure conforms to one or other of the 230 types of homogeneous structure which Schoenflies, Fedorov, and Barlow united in specifying as those alone possible to crystals. The facts are concisely expressed as follows : " Direct experimental proof is afforded that the structural units, the component chemical atoms and their molecular or polymolecular groups, are arranged in crystals in one or other of the 14 space-lattices as regards the main grosser structure (that of points representative of the molecule or small group of molecules), and in one or other of the 230 point-systems as regards the ultimate units, the chemical atoms themselves. . . . Indeed, it must happen that the structure revealed by X-rays shall agree with one of the 230 types of homogeneous structures which alone are possible to crystals." These words, quoted from the second edition of the writer's book [10] published early in the year, page 705 of Vol. I, are thus now by the year's work more than ever confirmed.

It is consequently of the highest importance for workers in the X-ray field of research to have before them a clear presentment of the 230 types. They are only in the simpler cases hard-and-fast stereotypes ; for the great majority permit of considerable variety in the details of the arrangement of the ultimate units (atoms), and it is the quite feasible task of the X-ray investigation to discover these details. The 65 (of the 230) more fundamental point-systems of Sohncke, to which or to their special cases most of the structures yet elucidated correspond (some of these special cases being simple space-lattices themselves), involve only coincidence movements or symmetry elements of the first order (rotations about axes, possibly screw axes, and translations), the other more rarely natur-

[10] A. E. H Tutton, " Crystallography and Practical Crystal Measurement." Second edition in two volumes, Macmillan & Co., 1922.

ally occurring 165 types involving also operations and symmetry elements of the second order (symmetry planes, mirror-image-reflection planes, mirror-axes, inversions, or symmetry centres). The 65 Sohncke point-systems are all described and illustrated, with exact reproductions of Sohncke's drawings, in the writer's book just referred to, pages 601 to 621. The special cases are also described in which the point-system becomes reduced directly to one of the 14 space-lattices of Bravais, and the derivation of the other 165 point-systems from the 65 is traced, and a table given showing the distribution of the whole 230 among the 32 crystal classes and seven crystal systems, with the Schoenflies class symbols and his space-group numbers. The details of the symmetry of all the 230 space-groups have been given by all three of the original independent discoverers, but the notation of Schoenflies, as given in his "Krystallsysteme und Krystallstructur," published in Leipzig in 1891, has become more generally adopted. An excellent summary of it is given by H. Hilton in his "Mathematical Crystallography," published in Oxford in 1903. P. Niggli has more recently, in his "Geometrische Krystallographie des Discontinuums" (Leipzig, 1919), given a considerable number of special cases of the space-groups, and has specified the positions within the unit cell of each space-group of all its symmetry elements.

H. Hilton, in a paper [11] to the Mineralogical Society in June last, refers to the bewildering variety of other suggested notations than that of Schoenflies, and points out that the Schoenflies notation itself suffers from two serious drawbacks. The first is that rotation and rotatory reflection are taken as fundamental operations, whereas for crystal-structure purposes rotation and rotatory inversion are needed. The second is that it is troublesome and expensive to print, involving small index and suffix numbers or letters after the capital letter symbol. He therefore suggests yet another notation, involving only English type and nothing above or below the line.

In October last a memoir of 180 pages in book form by R. W. G. Wyckoff [4] was published by the Carnegie Institute of Washington, in which all the special cases of the space-groups have been worked out. The matter contained is largely tabular, giving the co-ordinates of the most generally placed equivalent points and all the special cases of these equivalent points, contained within the unit of structure of each of the 230 space-groups. In this form the information will be immediately available to X-ray analysts. For a review of all the X-ray analyses yet carried out has shown that the number of particles (atoms) contained in the unit cell is

[11] H. Hilton, *Min. Mag.*, 1922, 19, 319.

usually smaller than the number of most generally placed equivalent points of the space-group having the symmetry of the crystal. The special arrangements of the equivalent points (on axes, planes, or other symmetry elements), whereby the number of symmetry elements is reduced, are thus of great importance to the X-ray analyst. This book is, therefore, one of very considerable value. Reference has, however, been already made to one point which it would be a clear advantage to remedy in any future edition of the work, namely, the replacement of the term " crystal molecule " by " crystal unit," which is really what Wyckoff means by the term. As Sir William Bragg remarks in a letter to the writer, the term " crystal molecule " is much better left to indicate the chemical molecule as it exists in the crystal unit, which latter is usually, as already so clearly proved, composed of more than one chemical molecule. For it is, indeed, most essential to discriminate between three very different things, the crystal unit, the crystal molecule, and the chemical molecule. By the latter is to be understood the molecule as it exists in the gaseous or liquid condition.

Miscellaneous X-*Ray Results.*

An important paper by M. Siegbahn,[12] on the improvements which he has introduced into X-ray spectrometry, gives some remarkably accurate determinations, suitable for use as *Standards of Reference,* of the angle of reflection of the first-order K_a radiation of copper from calcite. They are as follows :

With crystal face polished.				With rough cleavage face.		
14°	42′	2·8″		14°	42′	0·0″
14	41	59·8		14	41	59·9
14	41	59·6		14	41	59·2
14	42	1·3		14	41	58·0
14	41	59·5		14	41	59·6
14	42	2·3		14	42	5·5
Mean 14°	42′	0·8″		Mean 14°	42′	0·4′

The difference for the two conditions of face being so minute, the final mean 14° 42′ 0·6″ may be taken as a standard value. We have here an excellent proof that it is the inner planes within the crystal substance that are chiefly concerned in contributing to the reflection, and not the surface of the crystal face.

A Modification of the Powder Method was described by E. A. Owen and G. D. Preston to the Physical Society on December 8th, 1922, in which plates of aluminium, iron, copper, lead, and magnesium were examined on the Bragg X-ray spectrometer, employing radiation direct from a molybdenum anticathode. Excellent

[12] *Compt. rend.,* 1921, 178, 1350; *A.,* ii, 104.

spectra were obtained, which enabled the structure of these metals to be readily determined. Sir William Bragg pointed out that one of the planes becomes unduly accentuated by the polishing process, and this has to be remembered in interpreting the results.

The Structure of Ice.—In the last Report the work of D. M. Dennison was recorded, who found ice to have the structure of a close-packed hexagonal lattice, composed of two sets of interpenetrating triangular prisms, with edges 4·52 and height 7·32 Å.U., the axial ratio being $a : c = 1 : 1·62$. Sir William Bragg,[13] revising this work and the earlier work of A. St. John, finds that four such lattices interpene-

FIG. 10.

7·34 AU

4·52 AU
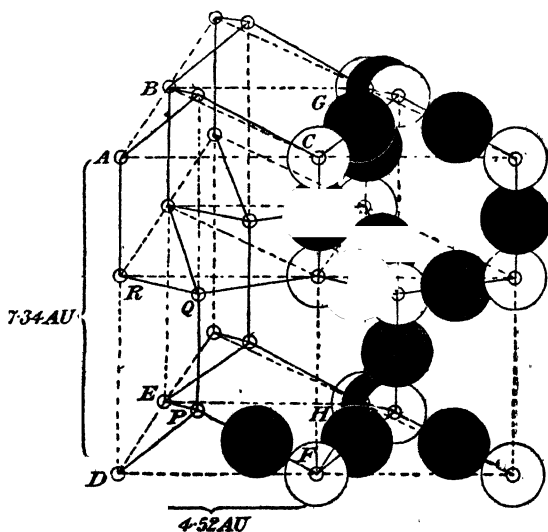
The Structure of Ice.

trate to form the complete structure, and confirms Dennison's figures for the dimensions. Each oxygen atom is at the centre of gravity of four neighbouring equidistant oxygen atoms, from each of which it is separated by a hydrogen atom, there being twice as many hydrogen atoms round each oxygen atom as there are oxygen atoms round each hydrogen atom. The structure is shown in Fig. 10.

The structure is an extremely open one, corresponding to the low density 0·9165, and it is easy to suppose that loose H_2O molecules, liquid water, would occupy less space, so that the expansion on freezing, and the melting of ice by pressure, is accounted for. The dimensions of the hydrogen atom are here measured for the first time, the sum of the diameters of oxygen and hydrogen atoms being 2·76 Å.U. As the diameter of the oxygen atom is 1·30, that of

[13] *Proc. Phys. Soc.*, 1922, **34**, 98.

hydrogen will be 1·46 Å.U. This is not too large, for G. Aminoff [14] has calculated it from investigations of magnesium and manganese hydrides as 2·16, and from the structure of ice as 2·24. From its relation to the alkali metals hydrogen might well be expected to have this slightly larger diameter than oxygen.

Structure of the Crystallised Elements.—A. W. Hull [15] has published two papers since the last report, regarding further results with his powder method. Summarising, cobalt, nickel, rhodium, palladium, iridium, platinum, and thorium have the face-centred cube structure. Iron has the centred cube structure. Ruthenium and osmium have hexagonal close-packed structures, the axial ratio of each being 1·59. Titanium, zirconium, and cerium have distorted hexagonal close-packed structures, with axial ratios 1·59 in the first two cases and 1·62 in the case of cerium.

L. W. McKeehan [16] has determined the structure of potassium cooled to −150°, and found the atoms to be arranged on a centred-cube lattice, with $a = 5\cdot20$ Å.U. The observed crystalline structure does not persist as the metal is allowed to regain room temperature. He has also investigated crystallised glucinum and found that it resembles magnesium, zinc, and cadmium (close-packed hexagonal) rather than calcium, strontium, and barium. There are two symmetrically interpenetrating hexagonal space-lattices, the side being 2·283 Å.U.

The crystal structure of germanium has been determined by N. H. Kolkmeyer [17] by the powder method, and found to resemble that of diamond, and the similar forms of silicon and tin. The lattice parameter $a = 5\cdot61$ Å.U.

Iron in its various forms has been studied by A. Westgren and A. E. Lindh, [18] and also by Westgren and G. Phragmen. [19] For pure iron (α-iron) Hull's result is confirmed, namely, a centred-cube lattice. Between 800° and 836°, within the β-iron region, the atomic grouping remains the same. They regard allotropy and polymorphism as synonymous, and that β-iron is only a particular modification of α-iron. Austenite and pure iron at 1000° were found to have a face-centred cube lattice, which is also characteristic of γ-iron. Hence the two really different forms are α- and γ-iron. Martensite was found to be α-iron, as was also high-speed tool steel

[14] G. Aminoff, *Geol. För. Förh.*, 1921, **43**, 389; *A.*, ii, 496.

[15] A. W. Hull, *Physical Rev.*, 1921, **18**, 88; *J. Franklin Inst.*, 1922, **193**, 189; see also *A.*, ii, 624.

[16] L. W. McKeehan, *Proc. Nat. Acad. Sci.*, 1922, **8**, 254, 270; *A.*, ii, 709.

[17] N. H. Kolkmeyer, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 125; *A.*, ii, 713.

[18] A. Westgren and A. E. Lindh, *Z. physikal. Chem.*, 1921, **98**, 181; *A.*, ii, 152.

[19] A. Westgren and G. Phragmen, *ibid.*, 1922, **102**, 1; *A.*, ii, 711.

hardened at 1275°. Iron wire at 800°, 1100°, and 1425°, within the β and γ regions, has the centred-cube structure like α-iron. The transition which occurs at 900° (A_3) is reversed at 1400° (A_4). The presence of carbon extends the space-lattices. Cementite and spiegeleisen crystals were found to be identical, of rhombic symmetry with four molecules of Fe_3C to the crystal unit.

Lithium Hydride has been studied by J. M. Bijvoet and A. Karssen,[20] and found to be cubic with four molecules of LiH to the crystal unit, the side of which is $a = 4·10$ Å.U., the structure resembling that of rocksalt.

Silver Oxide, which crystallises in small octahedra, has been investigated by the powder method by R. W. G. Wyckoff,[21] and found to resemble cuprous oxide, with a unit cube containing two molecules of Ag_2O, and an edge of 4·768 Å.U.

Magnesium Oxide has been reinvestigated by W. Gerlach and O. Pauli [22] by the powder method, and found to be constructed on a face-centred cube lattice, with length of side 4·22 Å.U., identical with the previous value.

Glucinum Oxide has been investigated by L. W. McKeehan,[22a] who finds the diffracting centres to lie at the points of two symmetrically interpenetrating hexagonal space-lattices having the side 2·696 Å.U.

Alkali Halides.—Ammonium chloride has been studied by R. W. G. Wyckoff [23] by the spectrometric and powder methods (first paper) and by the Laue radiographic method (second paper), and he has decided for tetrahedral and not plagihedral symmetry, the unit cube having only one molecule contained in it. The chlorine atoms are situated at the cube corners, the nitrogen atom at the cube centre, and the four hydrogen atoms are arranged tetrahedrally around and near the nitrogen atom. The side of the unit cube is 3·859 Å.U.

For this work some excellent crystals, clear rectangular prisms several millimetres in size, were obtained, from solutions containing urea. They afforded a refractive index of 1·639, and gave excellent Laue radiograms.

Lithium chloride, bromide, and iodide, and sodium, potassium, rubidium, and cæsium fluorides have been investigated by E. Posnjak and R. W. G. Wyckoff,[24] and the results, together with

[20] J. M. Bijvoet and A. Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 26; *A.*, ii, 569.

[21] R. W. G. Wyckoff, *Amer. J. Sci.*, 1922, [v], **3**, 184; *A.*, ii, 291.

[22] W. Gerlach and O. Pauli, *Z. Physik*, 1921, [vii], **2**, 116.

[22a] L. W. McKeehan, *Proc. Nat. Acad. Sci.*, 1922, **8**, 254, 270; *A.*, ii, 709.

[23] R. W. G. Wyckoff, *Amer. J. Sci.*, 1922, [v], **3**, 177; **4**, 469; *A.*, ii, 290.

[24] E. Posnjak and R. W. G. Wyckoff, *J. Washington Acad. Sci.*, 1922, **12**, 248; *A.*, ii, 499.

those of former work, are tabulated for twenty salts of the type RX. All prove to be of rocksalt type with simple cubic lattice, except cæsium chloride, bromide, and iodide, which possess the centred-cube lattice structure.

In the writer's opinion, this difference of structure on the part of the cæsium halides at once explains why a clear progression in crystallographic constants and properties is not manifested by the potassium, rubidium, and cæsium salts of halogen acids, similar to that which characterises the sulphates. The cæsium halides are obviously not strictly comparable with the corresponding potassium and rubidium halides.

W. P. Davey and Miss F. G. Wick [25] also find cæsium chloride to be constructed on a cubic lattice, with cæsium atoms at the corners and a chlorine atom at the centre of each cube. The spacings for the cube planes are for KCl 6·26 (Bragg), for RbCl 6·60 (Wyckoff), and for CsCl 4·12 Å.U. (Davey and Wick), the latter body-centred cube value being thus quite different from the values for the former two rocksalt groupings.

Cuprous Chloride, Bromide, and Iodide have been studied by R. W. G. Wyckoff [26] and prove to have the zinc blende arrangement of atoms in their crystals, the lengths of the sides of the unit cubes being respectively 5·49, 5·82, and 6·10 Å.U.

Potassium Cyanide has been examined by R. M. Bozorth,[27] using all three methods (of Laue, Bragg, and Debye). A structure somewhat similar to that of rocksalt is indicated, with potassium atoms at the sodium positions and the carbon and nitrogen atoms near the chlorine atomic positions, and 1·15 Å.U. apart, equidistant in each case from the chlorine position in rocksalt.

Cadmium Iodide has also been examined by Bozorth [27a] and found to be trigonal and not, as supposed, hexagonal. The crystal unit contains one molecule CdI_2, and the shortest distance between the centres of the cadmium and iodine atoms is 3·00 Å.U., which is exactly the sum of the radii given by W. L. Bragg.

The Aragonite Group of Minerals (aragonite, strontianite, witherite, and cerussite) forms the subject of a paper by M. L. Huggins,[28] who suggests that each carbon atom, as in calcite, is linked by double bonds to three oxygen atoms, each oxygen atom to two calcium atoms and one carbon atom, and each calcium atom to six oxygen

[25] W. P. Davey and Miss F. G. Wick, *Physical Rev.*, 1921, **17**, 403.

[26] R. W. G. Wyckoff and E. Posnjak, *J. Amer. Chem. Soc.*, 1922, **44**, 30; *A.*, ii, 295.

[27] R. M Bozorth, *ibid.*, 317; *A.*, i, 441.

[27a] *Ibid.*, 2232; *A.*, ii, 857.

[28] M. L. Huggins, *Physical Rev.*, 1922, **19**, 354; *A.*, ii, 463.

atoms, at the corners of an irregular octahedron (presumably a rhombic pyramid).

The Group of Isomorphous Nitrates of lead, barium, strontium, and calcium, $R(NO_3)_2$, crystallising in the tetrahedral pentagonal dodecahedral class 28 of the cubic system, has been studied by L. Vegard [29] by the powder method. The metallic atoms are arranged in a face-centred lattice; three oxygen atoms and one nitrogen atom form a group at four of the corners of a cube, this group having a trigonal axis and being surrounded by four metallic atoms.

Sodium Chlorate and Bromate, which also crystallise with class 28 symmetry, have been reinvestigated by R. G. Dickinson and E. A. Goodhue.[30] The atoms appear to be arranged with the symmetry of the Schoenflies space-group T^4, all the oxygen atoms being equivalent.

Phosphonium Iodide, PH_4I, has been submitted by R. G. Dickinson [31] to both the Bragg and Laue methods of X-ray analysis, and found to afford a similar structure to ammonium chloride at low temperatures. The unit cell has the dimensions 6·34 by 6·34 and 4·62 Å.U.

Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$, has been examined by the Laue method by R. W. G. Wyckoff and E. Posnjak,[32] and appears to have a structure resembling that of fluorspar, in which the $PtCl_6$ groups replace the calcium atoms, and the ammonium groups replace the fluorine atoms. The crystal unit cubic cell has a side of 9·843 Å.U. Curiously enough, Wyckoff [33] also finds that the crystals of the complex nickel ammonia compounds of the type $NiX_2,6NH_3$, formed when ammonia is added to solutions of nickel chloride, bromide, and iodide respectively, are arranged in a similar manner isomorphous with ammonium chloroplatinate, the sides of the unit cells in the three cases being 10·09, 10·48, and 11·01 Å.U. In each case there are four molecules in the crystal unit cell, the nickel atoms replacing those of platinum, and the nitrogen atoms occupying the positions of the chlorine atoms.

Potassium Chloroplatinate, $K_2[PtCl_6]$, and the salts $Rb_2[PdBr_6]$ and $[Ni(CH_3)_6]Cl_2$ have also been investigated by P. Scherrer and P. Stoll [34] and found to resemble fluorspar and ammonium chloroplatinate, the co-ordinated complex in square brackets replacing the calcium.

[29] L. Vegard, *Z. Physik,* 1922, **9**, 395; *A.,* ii, 503.

[30] R. G. Dickinson and E. A. Goodhue, *J. Amer. Chem. Soc.,* 1921, **43**, 2045; *A.,* ii, 145.

[31] R. G. Dickinson, *ibid.,* 1922, **44**, 1489; *A.,* ii, 640.

[32] R. W. G. Wyckoff and E. Posnjak, *ibid.,* 1921, **43**, 2292; *A.,* ii, 214.

[33] R. W. G. Wyckoff, *ibid.,* 1922, **44**, 1239; *A.,* ii, 573.

[34] P. Scherrer and P. Stoll, *Z. anorg. Chem.,* 1922, **121**, 319; *A.,* ii, 524.

Ammonium Fluosilicate has been structurally analysed by X-rays by R. M. Bozorth,[35] and found also to resemble ammonium chloroplatinate, ammonium chlorostannate, and potassium chlorostannate, namely, in possessing the type of structure of fluorspar, the fluorine atoms of the latter being replaced by an ammonium group, and each calcium atom by a fluosilicate group, with the six fluorine atoms equidistant from the silicon atom in the direction of the crystal axis. The unit cube contains four molecules of $(NH_4)_2SiF_6$ and the side measures 8·38 Å.U. The sides of the other three compounds mentioned are respectively 9·84, 10·05, and 9·96 Å.U.

Silver Molybdate has been examined by R. W. G. Wyckoff [36] by both the X-ray spectrometric and the radiographic methods, and found to possess a structure like that of magnetite and the spinels, with eight molecules to the unit cube, which has a side of 9·26 Å.U.

X-Radiograms of Strained Crystals have been studied by A. F. Joffe and M. V. Kirpitcheva.[37] In the case of rocksalt, gradually loaded by means of an electromagnet, when the limit of elasticity is passed the Laue spots elongate, and even before it is reached the spots elongate and break up into stratifications, increasing in number with the strain, due to different small crystals into which the crystal breaks up, each of the same structure as the original crystal. The molecules glide along the plane of the rhombic dodecahedron and also rotate. The method is suitable for determining the limit of elasticity, and the mode of destruction. A method is also described which gives on two photographs the strains in every direction, and enables all the constants of elasticity to be determined from one small crystal.

Crystallographic Chemical Investigations.

The last two papers of the writer's research on the hexahydrated double selenates were read to the Royal Society on March 14th last, and published shortly afterwards.[38] They relate to the manganese and cadmium groups of double selenates. Sufficient was said in last year's report (pages 231 to 234) concerning this prolonged investigation—which includes not only this large group of monoclinic double salts, $R_2^S M(SeO_4)_2,6H_2O$, but also the simple rhombic normal sulphates and selenates of the alkalis, $R_{2Se}^S O_4$,

[35] R. M. Bozorth, *J. Amer. Chem. Soc.*, 1922, **44**, 1066; *A.*, ii, 499.

[36] R. W. G. Wyckoff, *ibid.*, 1994; *A.*, ii, 765.

[37] A. F. Joffe and M. V. Kirpitcheva, *Phil. Mag.*, 1922, [vi], **43**, 204.

[38] A. E. H. Tutton, *Proc. Roy. Soc.* 1922, [*A*], **101**, 225, 245; *A.*, ii, 502, 505.

75 salts in all having been very fully dealt with—to render more than passing notice in this Report superfluous. It will suffice to say that at the conclusion of the second (last) memoir, that on the cadmium group, six pages are devoted to a general review of the whole research, and are followed by a complete list (with references) of the separate memoirs, 26 in number, in which the results have from time to time been communicated, and of six others describing the new instruments devised for the work. The two main results which stand out are (1) the progression of the whole of the crystallographic and physical constants with the atomic number of the alkali metal, potassium, rubidium, or cæsium, and (2) the iso-structure of the analogous rubidium and ammonium salts. But even the many minor results are proving of more than passing interest in the light of other contemporary research, especially that concerning the structure of the atom and that brought about by the advent of X-ray crystal analysis; and it is highly satisfactory that there is full agreement between all this that is fully substantiated and the writer's results. A quotation of the last paragraph of the final paper will perhaps best express it.

" Thus it has come about, by the time that the author has completed his crystallographic investigation of these important isomorphous series, that a full explanation of the results is afforded by the immense amount of real knowledge that has been accumulated during the same time concerning the structure and nature of the chemical atom, and that revealed by means of X-rays, from which the law of atomic diameters has been derived. It is thus highly satisfactory that the work of Moseley, Sir J. J. Thomson, Langmuir, the Braggs and the author should so perfectly agree in giving us a wider and fuller understanding of the nature of crystals, and of the structure of the solid matter of which they are the organised expression, than could have been expected or anticipated at the time when the author's researches on these isomorphous series were initiated."

The Dissociation Pressures of Hydrated Cupric Alkali Sulphates is the subject of an interesting paper by R. M. Caven and J. Ferguson.[39] The salts investigated were the copper group of double sulphates, $R_2SO_4,CuSO_4,6H_2O$, in which R is potassium, rubidium, cæsium, ammonium, or thallium. The results agree with the writer's conclusion in the research just referred to, that there is a clear increase in the electropositive character of the alkali metal in passing from potassium, through rubidium, to cæsium. They are expressed in the curves reproduced in Fig. 11. They indicate that the water of crystallisation is held more firmly, the greater the electropositive-

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[39] R. M. Caven and J. Ferguson, *T.*, 1922, **121**, 1406.

ness of the alkali metal, and also that the heat evolved in the combination of the lower hydrate (with $2H_2O$) with water also increases as the electropositive character of the alkali metal advances in

FIG. 11.

⊙ *Ascending temperature.* ✕ *Descending temperature.*
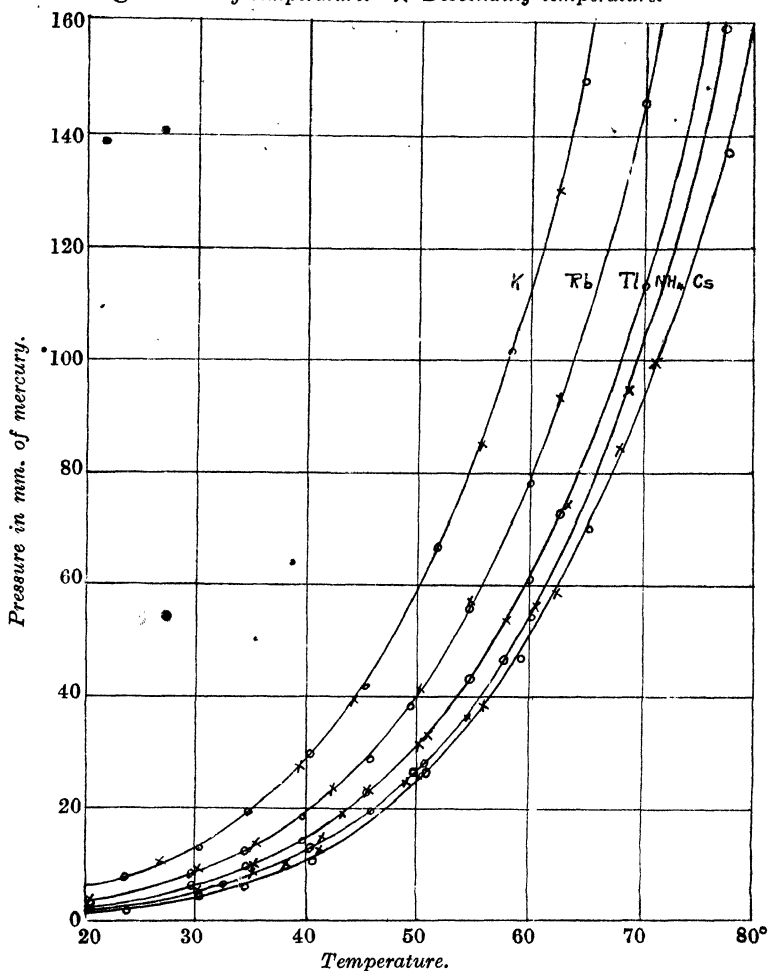
Vapour Pressures of Copper Group of Double Sulphates.

strength. Moreover, the affinity of the process shows very markedly the same variation. The positions of thallium and ammonium relative to rubidium and caesium in the series of alkali metals, as determined by these experiments, accord with those assigned to them by the writer from observations of the morphological and

physical properties of their salts. This practically verbatim quotation from the conclusions of Caven and Ferguson forms a welcome confirmation from a new standpoint.

A Crystallographic and Optical Study of some Inorganic Complex Salts has been made by Miss Isabel E. Knaggs.[40] The first of the substances dealt with is potassium ferri-oxalate, $[Fe(C_2O_4)_3]K_3,3H_2O$, which crystallises with holohedral monoclinic symmetry and has been already investigated by F. M. Jaeger, with whose data this new measurement agrees. The second substance is the analogous aluminium compound, in which aluminium replaces the iron, and which is shown to be truly isomorphous. A number of still more complicated compounds having *cis-* and *trans-* forms were investigated, and some rather surprising cases of apparent isomorphism observed.

At the meeting of the Mineralogical Society on November 7th, 1922, Miss Knaggs also gave an account of the crystals of some interesting carbon compounds of the four types CX_4, CX_3Y, $C(CX_3)_4$, and $C(CX_2Y)_4$, where X and Y are other elements. Those of the first and third types, containing only one other element than carbon, appear to be usually cubic, while those of type 2 are trigonal or hexagonal, and those of type 4 tetragonal. The symmetry of the crystal thus resembles to a considerable extent that of the molecule, suggesting that there may be only one molecule in the crystal unit in these cases of more symmetrical molecules. It will be highly interesting to have these cases investigated by means of X-rays, so as to ascertain whether this is really the case, especially in the light of Shearer's rules.

Physical-crystallographic Investigations.

The Piezo-electricity of Rochelle Salt forms the subject of a paper by E. K. Scott.[41] Some large crystals, weighing 100 grams or more, were used, and the piezo-electric effect was very pronounced when they had received prolonged drying, first with alcohol and subsequently at 40°. Crystals showing " hour-glass " marking afforded the effect best of all, by the application of a twisting couple about the principal axis of the crystals. Potentials as high as 500 volts were developed. The crystals may be used for the reproduction and transmission of sounds.

A New Optical Property of Biaxial Crystals has been observed by C. V. Raman and V. S. Tamma,[42] using a plate of aragonite cut perpendicular to the acute bisectrix of the optic axial angle.

[40] (Miss) Isabel E. Knaggs, *T.*, 1922, **121**, 2069.
[41] E. K. Scott, *Trans. Faraday Soc.*, 1922, **17**, 748; *A.*, ii, 609.
[42] C. V. Raman and V. S. Tamma, *Phil. Mag.*, 1922, [vi], **43**, 510.

Although the object used is a plate bounded by parallel faces, it forms a real erect image, with unit magnification, of a pinhole or other small source or object, illuminated with monochromatic light. If white light be used, a spectrum is afforded.

A luminous filament may be used instead of a pinhole, to vary the phenomena. The image is formed by light which travels through the crystal along an axis of single ray velocity.

The Sizes of Atoms in Crystals.—The values given by W. L. Bragg for the diameters of the atoms of such elements as have yet entered into crystals examined by X-rays, from which he deduced his important law of atomic diameters, and which were quoted on page 229 of the last Report, have on the whole been remarkably confirmed by work published during 1922. Thus R. N. Pease[43] finds the following interatomic distances, the values of Bragg being given afterwards in brackets : in diamond 1·54 (1·54), in silicon 2·30 (2·35), in grey tin 2·80 (2·80), in silicon carbide 1·92 (1·90), in zinc blende 2·41 (2·35), and in cuprous chloride 2·41 (2·43). Also an investigation of the viscosity of silicon hydride, SiH_4, by A. O. Rankine and C. J. Smith[44] has yielded further confirmation and support.

New Minerals.

Quite a considerable number of new minerals have been announced during the year 1922, of which the following may be mentioned, including a rich find of radioactive minerals at Katanga in the Belgian Congo.

Becquerelite, described by A. Schoep,[45] is a radioactive mineral occurring at Katanga as yellow crusts of small orthorhombic crystals on pitchblende. It contains 86·5 per cent. of UO_3, and is practically $UO_3,2H_2O$.

Dewindtite, also described by Schoep,[46] was also found at Katanga, and is a radioactive yellow powder of the composition

$$4PbO,8UO_3,3P_2O_5,12H_2O.$$
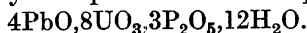
Soddite, also a radioactive mineral from Katanga described by the same author,[47] occurs as orthorhombic crystal aggregates of the composition $12UO_3,5SiO_2,14H_2O$.

Stasite, found at Kasola, Katanga, again described by Schoep,[48] has the same composition as dewindtite, the substance being di-

[43] R. N. Pease, *J. Amer. Chem. Soc.*, 1922, **44**, 769; *A.*, ii, 428.

[44] A. O. Rankine and C. J. Smith, *Proc. Physical Soc.*, 1922, **34**, 181; *A.*, ii, 709.

[45] A. Schoep, *Compt. rend.*, 1922, **174**, 1240; *A.*, ii, 450.

[46] *Idem, ibid.*, 623; *A.*, ii, 305.

[47] *Idem, ibid.*, 1066; *A.*, ii, 451.

[48] *Idem, ibid.*, 875; *A.*, ii, 386.

morphous. It occurs as golden-yellow, flat prisms, and also differs in density from dewindtite, as well as in crystal form and in colour.

Ceruleofibrite, described by E. F. Holden,[49] is a basic chloro-arsenate of copper, $CuCl_2,\tfrac{1}{3}Cu_3As_2O_8,6Cu(OH)_2$, which was found as radiating tufts of bright blue fibres, orthorhombic needles, on cuprite from Arizona.

Gillespite, described by W. T. Schaller,[50] was found in an Alaskan moraine as scaly masses, and appears to have the composition $Fe''BaSi_4O_{10}$.

Sincosite, also described by Schaller,[51] is a hydrous calcium vanadyl phosphate, $CaO,V_2O_4,P_2O_5,5H_2O$, from Sincos, Peru. It forms uniaxial plates belonging to the uranite group.

Melanovanadite, described by W. Lindgren, L. F. Hamilton, and C. Palache,[52] occurs as bunches of black, monoclinic needles on a black shale from Minasragra, Cerro de Pasco, and has the composition $2CaO,3V_2O_5,2V_2O_4$.

Thorveitite is a silicate of scandium found at Sætersdalen, Norway, in large, greyish-green, monoclinic prismatic crystals resembling epidote. It appears to be $(Sc,Y)_2Si_2O_7$, analogous to thalenite. It was discovered and described by J. Schetelig.[53]

New Books and Editions.

Prof. F. Rinne (Leipzig) has produced during 1922 new editions of his two books " Das feinbauliche Wesen der Materie nach dem Vorbilde der Kristalle," published by Gebrüder Borntraeger, Berlin, and " Kristallographische Formenlehre und Anleitung zu kristallographisch-optischen röntgenographischen Untersuchungen," published by Max Janecke, Leipzig. The former contains excellent portraits of von Groth, Haüy, Schoenflies, Fedorov, Tschermak, von Laue, Debye, Scherrer, Sir W. H. Bragg, and W. L. Bragg. It is full of illustrations and diagrams of an original character, including many of Prof. Rinne's own X-radiograms of crystals. It regards the whole achievement of X-ray analysis as having revealed the true nature of the fine structure of solid matter. The second and later book is also very original inasmuch as it gives a readable account of crystal phenomena and ordinary elementary Crystallography from the aspect of one steeped in the later X-ray analytical work.

In July there was published by Thomas Murby & Co. a book of 152 pages by Mr. T. V. Barker, Lecturer in Chemical Crystallo-

[49] E. F. Holden, *Amer. Min.*, 1922, **7**, 80; *A.*, ii, 516.

[50] W. T. Schaller, *J. Washington Acad. Sci.*, 1922, **12**, 7.

[51] *Idem, ibid.*, **12**, 195; *A.*, ii, 450.

[52] W. Lindgren, L. F. Hamilton, and C. Palache, *Amer. J. Sci.*, 1922, [v], **3**, 195; *A.*, ii, 305.

[53] J. Schetelig, *Norsh. Geol. Tidsskr.*, 1922, **6**, 233; *A.*, ii, 306.

graphy at Oxford, on " Graphical and Tabular Methods in Crystallography." In it are described the methods of crystallographic practice which Mr. Barker has made his own, largely following the methods of V. Goldschmidt and Fedorov, especially those involving rapidity of work and concise expression. It is a most valuable compendium of the more recent and useful graphical methods.

A so-called " third " edition by W. E. Ford of Dana's " Text Book of Mineralogy," with an extended treatise on crystallography and physical mineralogy, has been published in New York. It forms a rejuvenated, very much enlarged, and fairly up-to-date revision of the great text book of 1877, the total issues of which in its many editions and re-issues are estimated to have reached 27,000.

The second edition of the writer's " Crystallography and Practical Crystal Measurement " was published by Messrs. Macmillan and Co. in March, in two volumes of 760 and 686 pages respectively, the first edition having been comprised in one volume of 946 pages. Each volume is in two parts, the total of 60 chapters being thus divided into four parts These are : Part I, Crystal Form and Goniometry; Part II, Crystal Structure and its X-Ray Analysis; Part III, Crystal Optics and Microscopy; and Part IV, Crystal Chemistry, Deformational Physics and its Interferometry.

A ninth List of new Mineral Names by Dr. L. J. Spencer, was issued in 20 pages with the September number of the *Mineralogical Magazine*. A concise description is given of each of the minerals included. Mineralogists and crystallographers are again indebted to Dr. Spencer not only for this further most useful, long list, but, with some assistance from collaborators, for the *Mineralogical Abstracts*, which are now regularly issued by the Mineralogical Society, with the *Mineralogical Magazine*. Volume I of these Abstracts, just completed, contains no fewer than 1254 abstracts, extending from the year 1915 to 1922. In spite of the considerable cost entailed by their publication, it is very satisfactory that the Society has decided to continue this most valuable addition to the magazine.

Concluding Remarks.

In concluding this epitome of the crystallographic and mineralogical work of the year 1922, mention should be made of the highly interesting special number of " Die Naturwissenschaften " entitled " Zehn Jahre Laue-Diagramm," which was issued in April, containing eight articles by authors who have contributed to the subject of the X-ray analysis of crystals since its inception by Dr. M. von Laue in the year 1912. They include Prof. von Laue's collaborators

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in the first discovery, Drs. Friedrich and Knipping. The former gives a most interesting account of the circumstances of the original discovery, in the midst of the remarkable coterie of experts at that time in Munich, which included Röntgen, von Groth, Ewald, Sommerfeld, and Laue. The origin appears to have been a discussion between Laue and Ewald as to how the minuter electromagnetic waves would behave with gratings of a similar small order of dimensions, and an enthralling description is given of the excitement among the whole scientific circle at Munich when the experiment was tried by Friedrich and, after a preliminary failure owing to not having hit off the right conditions, so admirably succeeded, and the diffraction or reflection of X-rays by the planes of atoms in crystals became an accomplished fact. Indeed, the excitement was still high when, that same summer, both Fedorov and the writer visited von Groth at Munich, and were shown the first X-radiograms of zinc blende.

This Report is but a very inadequate attempt to do justice to the amount of valuable research which has been carried out during the year 1922. But sufficient will doubtless have been written to show that the tenth anniversary of the inauguration of this new weapon of research, and the centenary of Pasteur, the discoverer of the true nature of tartaric acid and of the meaning of its optical activity, is marked by a richness of result that the discoverers in the years 1912 and 1848 respectively could never have foreseen, still less have anticipated; and that the promise of a still richer harvest yet to be gleaned by the earnest workers of the future is so bright and alluring as to afford the highest encouragement to those who are making this branch of natural knowledge their special domain.

A. E. H. TUTTON.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.*

Introduction.

UNDER the title " Sub-atomic Phenomena and Radioactivity " are included in a broad sense all phenomena directly associated with the central nuclei of atoms, as opposed to the so-called chemical phenomena which we now know to be connected with the behaviour of the planetary electrons occupying the outer domains of these atoms. This Report will therefore be concerned with the masses of individual atoms determined by physical means, the isotopic constitution of the chemical elements, and their spectra, in so far as these are affected by isotopy. It will also deal with work on the constitution of the nuclei themselves and the manner in which they may be disintegrated artificially. All phenomena connected with the spontaneous disintegration of the more complicated nuclei are, of course, included in radioactivity.

During the past two years advances have been made in all these branches and some valuable steps taken towards elucidating the structure of the nucleus itself. Among the more important of these should be mentioned the studies on artificial disintegration and other phenomena of nuclear collision made by Rutherford and his colleagues, and the application of the quantum theory to explain the relation between β-rays and the γ-rays which produce them, by Ellis and others. Progress in this direction is also promised by the discovery of divergences from the whole-number rule, but the accuracy of comparison of atomic masses will have to be advanced considerably beyond that at present available before much information will be obtainable from this line of attack.

The Isotopic Constitution of the Elements.

The work in this field during 1921 has been already summarised in the Report for that year.[1] During 1922, several more elements have been successfully investigated and other additional results obtained. Dempster has applied his method of positive ray analysis to calcium and zinc, and the composition of five more elements has been determined by means of the mass-spectrograph. The theory of the latter instrument has been satisfactorily worked

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* This Report covers the years 1921 and 1922.

[1] *Ann. Rep.*, 1921, **18**, 34—35.

out mathematically [2] and a notable advance in its technique has been made by the use of specially treated photographic plates. These results are summarised below.

Aluminium.—Results obtained by the mass-spectrograph when pure chlorine was present in the discharge tube and had reacted with the aluminium electrodes leave very little doubt as to the constitution of this metal. Aluminium may be regarded as a simple element of atomic weight 27, as its chemical atomic weight would lead us to suspect.[3]

Calcium.—By the treatment of this metal in the same way as magnesium [4] Dempster [5] has been able to show that calcium has a principal isotope 40 with a weaker component 44.

Chlorine.—It is now reasonably certain that this element does not contain any appreciable quantity of an isotope 39.[6]

Iron.[7]—This element has been investigated by means of its volatile pentacarbonyl. Its mass-spectrum is characterised by a strong line at 56 and possibly a very faint one at 54. The measurements on the former indicate a value slightly less than a whole number, but the divergence is within the experimental error.

Zinc.—This metal was analysed by Dempster at the same time as calcium. The results indicate that it consists of four isotopes the masses of which, by comparison with the calcium line 40, are given as 64, 66, 68, and 70. The first appears the strongest component and the last is very feeble.

Selenium.[8]—The mass-spectra of selenium were obtained by a special device by which the element itself was vaporised in the discharge tube. The results were very definite and show that it consists of six isotopes 74, 76, 77, 78, 80, 82. Isotope 74 is only present in minute proportion. No divergence from the whole-number rule could be detected.

Tin.[9]—By the use of its volatile methide, this element has been shown to consist of seven, or possibly eight, isotopes, as given in the following table. Measurement of their masses indicates that, although their differences are integral to the highest accuracy, the masses themselves tend to be 2 to 3 parts in 1000 less than whole numbers on the oxygen scale. This is the first definite divergence observed since that of hydrogen, and it cannot be attributed to experimental error in measurement on the following account. The

[2] F. W. Aston and R. H. Fowler, *Phil. Mag.*, 1922, [vi], **43**, 514; *A.*, ii, 241.

[3] F. W. Aston, *Nature*, 1922, **110**, 664; *A.*, ii, 844.

[4] *A.*, 1921, ii, 402.

[5] *Physical Rev.*, 1922, **20**, 631.

[6] F. W. Aston, *Nature*, 1922, **110**, 664; *A.*, ii, 844.

[7] *Idem, ibid.*, 312; *A.*, ii, 710.   [8] *Idem, ibid.*, 664; *A.*, ii, 844.

[9] *Idem, ibid.*, **109**, 813; *A.*, ii, 650.

lines of xenon were present on the plate, hence the line 135 due to $Sn^{120}CH_3$ should have appeared exactly half-way between the two strong xenon lines 134 and 136. It was actually unmistakably nearer the former. Whether this large divergence, which is about 0·3 in atomic weight, represents the accumulated divergence of both elements, cannot be settled, although it is most probable that tin diverges more from a whole number than xenon. In any case, it is remarkable that it should occur in two elements so near in atomic number as tin and xenon.

Antimony.[10]—The mass-spectrum of antimony consists of two strong lines, 121, 123, the former being slightly the more intense. Very faint lines also appear at 122, 124, but these are ascribed to hydrides. The masses of the two isotopes of antimony are probably slightly less than whole numbers. The results show that the old value for the atomic weight, 120·2, is definitely wrong, but they are in good agreement with the value recently obtained by Willard and McAlpine.

Xenon.—The mean atomic weight of this element estimated from its mass-spectrum is distinctly higher than the accepted value obtained from the density by Moore.[11] In order to ascertain whether the discrepancy could be put down to the presence of krypton as an impurity, a sample of the actual gas used in the density determinations was analysed by means of the mass-spectrograph. The results showed no appreciable presence of krypton, so that the difference remains unexplained. The two doubtful isotopes, 128, 130, have been confirmed,[12] and two extremely faint probable additional ones have been detected at 124, 126.[13]

From the table of results on p. 270, some interesting statistical relations are at once apparent. In the nucleus of the atom there is never less than one electron to every two protons; in other words, the atomic weight of the lightest isotope of an element cannot be less than twice its atomic number, except in the case of hydrogen. The excess of the atomic weight over twice the atomic number has been called the isotopic number by Harkins. The number of isotopes of any one element shows definite limits and tends to increase with atomic number. It is also greater for elements of even than for those of odd atomic number; in the latter case, it is never greater than two. The number of electrons in the nucleus tends to be even, that is, in the majority of cases even atomic number is associated with even atomic weight and odd

[10] F. W. Aston, *Nature*, 1922, **110**, 732; *A.*, 1923, ii, 32.
[11] " Isotopes," p. 114.
[12] F. W. Aston, *Nature*, 1922, **109**, 813; *A.*, ii, 650.
[13] *Idem, ibid.*, **110**, 664; *A.*, ii, 844.

Table of Elements and Isotopes.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes in order of intensity.
H	1	1·008	1	1·008
He	2	3·99	1	4
Li	3	6·94	2	7, 6
Gl	4	9·1	1	9
B	5	10·9	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22
Na	11	23·00	1	23
Mg	12	24·32	3	24, 25, 26
Al	13	26·96	1	27
Si	14	28·3	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37
A	18	39·88	2	40, 36
K	19	39·10	2	39, 41
Ca	20	40·07	(2)	40, 44
Fe	26	55·84	(1)	56, (54) ?
Ni	28	58·68	2	58, 60
Zn	30	65·37	(4)	64, 66, 68, 70
As	33	74·96	1	75
Se	34	79·2	6	80, 78, 76, 82, 77, 74
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
Rb	37	85·45	2	85, 87
Sn	50	118·7	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Sb	51	121·77	2	121, 123
I	53	126·92	1	127
X	54	130·2	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
Cs	55	132·81	1	133
Hg	80	200·6	(6)	(197—200), 202, 204

(Numbers in brackets are provisional only.)

with odd. If we plot the first 40 natural numbers and show those occupied by known elements as in the figure, a curious relation
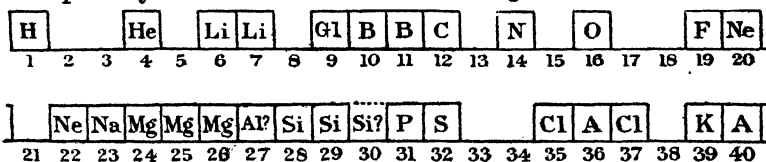
may be noticed, namely, that the simple recurring series 2, 3, 5, 8 – –, of which each term is the sum of the two previous terms, is in every case, up to 34, represented by a gap. This relation may break down at the next term, if manganese has an isotope 55, but this is not yet known.

Isobares.—These are substances having the same atomic weight

but different chemical properties. They have been well known for some years among the radioactive elements, but among the non-radioactive ones, although it was perfectly certain they must exist, none was actually observed until Dempster showed that the principal isotope of calcium had an atomic weight 40 and so was isobaric with the principal isotope of argon. Since then, the seleniums 78, 80, 82 have been found isobaric with kryptons, and one tin 124 with a probable xenon. If we disregard the doubtful isobaric pair Sb, Sn 121, every pair has for one of its members an inert gas, and all the isobares (including the radioactive ones) have atomic weights which are even numbers.

Periodic Systems of Elements and Isotopes.

Many new periodic systems of the elements have been put forward by Bourgerel,[14] Oddo,[15] Partington,[16] Kirchhof,[17] Masson,[18] Broek,[19] Kohlweiler,[20] and others. Some of these are worked out theoretically on some physical basis, for example, the purely speculative idea that all elements are the results of radioactive disintegrations. Others are convenient schemes of representing the numerical values obtained by experiment in such a way as to bring out certain interesting points. The most complete scheme of this kind is that of Harkins, which has been elaborated by him in numerous publications [21] to which the reader is referred. In a valuable table given in one of his most recent papers [22] is to be found a remarkably complete summary of the facts and reasonable speculations in this field. In this diagram, against their atomic numbers, are plotted the " isotopic numbers " of all atomic species known and probable. They lie in a band of roughly parabolic curvature which widens as it gets further from the origin. The probable constitutions of elements, not experimentally analysed at the time the scheme was drawn up, are admittedly speculative and dependent on the trustworthiness of the chemical atomic weight determinations. The accuracy of the predictions in the cases of selenium and antimony is very striking at first sight, and shows how much can be done by the judicious use of general and statistical relations such as those given in the previous paragraph.

[14] *Mon. Sci.*, 1920, **10**, 241; *A.*, 1921, ii, 102.
[15] *Gazzetta*, 1920, **50**, 213; *A.*, 1921, ii, 102.
[16] *Chem. News*, 1920, **121**, 304; *A.*, 1921, ii, 103.
[17] *Physikal. Z.*, 1920, **21**, 711; *A.*, 1921, ii, 103.
[18] *Phil. Mag.*, 1921, [vi], **41**, 281; *A.*, 1921, ii, 191.
[19] *Physikal. Z.*, 1921, **22**, 164; *A.*, 1921, ii, 295.
[20] *Ibid.*, 243; *A.*, 1921, ii, 689.
[21] *A.*, 1921, ii, 445, 583, 690; 1922, ii, 490, 702.
[22] W. D. Harkins, *J. Franklin Inst.*, 1922, **194**, 645.

The Constancy of Chemical Atomic Weight and the Relation of the Latter to the Mean Weight deduced from the Results of the Mass-spectrograph.

As soon as the isotopic nature of some common and widely distributed elements had been definitely proved, it became of interest to determine with the greatest care the atomic weights of such complex elements from sources as widely distributed as possible. Differences might be expected from two causes; either the process of origin of the element might be different at different points of the earth's surface, yielding isotopes in different proportions, or elements of the same original constitution might have their mean weight changed by some natural process which tended to bring about partial separation of the constituent isotopes. Several pieces of work have been performed with a view to test this point. Baxter and Parsons [23] compared the atomic weight of nickel from meteorites with that of ordinary terrestrial nickel, but no difference was found beyond that expected from experimental error. (Mlle) Curie has compared the atomic weight of chlorine from several minerals with that of chlorine from sea-water. In the case of two, the marine origin of which was in the highest degree unlikely, no difference was found. Chlorine prepared from a sample of sodium chloride obtained from a desert region in Central Africa gave a value slightly above normal.[24] Chlorine from an ancient mineral, apatite, from Balme has also been investigated [25]; no difference from normal chlorine could be detected. Taking into consideration the age and origin of the mineral, it may be concluded that the chlorine at the time of the formation of the minerals of the primary magma contained the two isotopes in the same proportion as it does to-day, or that the two isotopes were then formed in constant proportions.

Boron is an element well suited for this test, for its isotopes differ by 10 per cent. in mass and are both present in considerable proportion. Monro [26] has compared the atomic weight of boron from some New Zealand minerals with that of the element obtained from pure sodium borate; here again no difference could be detected. Finally, Brönsted and Hevesy [27] measured the density of mercury from minerals of different origin and found no divergence higher than that corresponding with a difference in atomic weight of 0·0004—0·0012.

[23] *J. Amer. Chem. Soc.*, 1921, **43**, 507; *A.*, 1921, ii, 338.

[24] Mlle Irene Curie, *Compt. rend.*, 1921, **172**, 1025; *A.*, 1921, ii, 396.

[25] Mlle Ellen Gleditsch and B. Samdahl, *ibid.*, 1922, **174**, 746; *A.*, ii, 281.

[26] T., 1922, **121**, 986.

[27] *Nature*, 1922, **109**, 813; *A.*, ii, 645.

The accumulation of negative evidence of this kind is very impressive, and supports the idea, already put forward, that the evolution of the elements (apart from those produced by radio-active disintegration) must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and since we know of no natural process of separation, has remained constant ever since.

Although no accurate determinations of the relative intensity of mass-spectrum lines has yet been carried out, their relative strengths can be approximately estimated. Hence the mean atomic weight of a complex element can be deduced in some cases with considerable accuracy, and therefore provides a valuable check on the figure obtained by the ordinary chemical methods. In most cases, the agreement has been good, but in a few the discrepancy is considerable.[28]   It is satisfactory to note that during the past year redeterminations of the chemical atomic weights have removed the discrepancy in several cases.   Thus the revision of the atomic weight of boron by two independent determinations [29] gives 10·83 and 10·82, respectively, figures agreeing much better with that estimated from the mass-spectrum, 10·75 ± 0·07, than did the previous values, 11·0 and 10·90.   Again, positive ray results [30] indicate that glucinum is a simple element, whereas the old value for the atomic weight, 9·1, differs so far from a whole number as virtually to deny this possibility.   This discrepancy has now been removed by the redetermination of the chemical atomic weight by Hönigschmid and Birckenbach,[31] who obtain a value 9·018.   The cases of antimony and xenon have already been alluded to, that of krypton is still unexplained.

Atomic Volume of Isotopes.—Soddy [32] has compared the values obtained for the density and atomic weight of ordinary lead, lead from thorite, and lead from uranium minerals.   He concludes that the atomic volumes cannot differ by so much as three parts in ten thousand and the atomic diameters by so much as one part in ten thousand.

The Spectra of Isotopes.

Series Spectra.—Merton has repeated his experiments on the isotopes shift of the line λ 4058 of lead [33] and extended his measure-

[28] See F. W. Aston, " Isotopes " (Arnold, 1922), p. 114.

[29] G. P. Baxter and A. F. Scott, *Science*, 1921, **54**, 524; *A.*, ii, 285; O. Hönigschmid and L. Birckenbach, *Anal. Fis. Quim.*, 1922, **20**, 167; *A.*, ii, 641.

[30] G. P. Thomson, *Phil. Mag.*, 1921, [vi], **42**, 857; *A.*, 1921, ii, 675.

[31] *Ber.*, 1922, **55**, [*B*], 4; *A.*, ii, 214.

[32] *Nature*, 1921, **107**, 41; *A.*, 1921, ii, 698.

[33] *Ann. Rep.*, 1920, **17**, 224.

ments to other lines. Using a very pure sample of uranium lead from Australian carnotite, he obtained the results indicated in the following table : [34]

λ	$\begin{bmatrix} \lambda\text{(Carnotite lead)} \\ -\lambda\text{(ordinary lead)} \end{bmatrix}$	$\begin{bmatrix} \text{Wave number (ordinary lead)} \\ -\text{Wave-number (carnotite lead)} \end{bmatrix}$
4058	0.011 ± 0.0008	0.065 ± 0.005
3740	0.0074 ± 0.0011	0.053 ± 0.008
3684	0.0048 ± 0.0007	0.035 ± 0.005
3640	0.0070 ± 0.0003	0.052 ± 0.002
3573	0.0048 ± 0.0005	0.037 ± 0.004

It will be noticed that the shift for the line λ 4058 is rather more than twice that obtained before. Merton suggests that the most probable explanation of this difference is that the carnotite lead used was a purer sample of uranium lead than that obtained from the pitchblende residues. It is also apparent that the differences are not the same for different lines, an interesting and somewhat surprising result.

McLennan and Ainslie [35] have subjected the light from a strong lithium arc to the highest resolution and find that the line λ 6708 consists of a close quartet with separations of 0·128 Å., 0·173 Å., and 0·165 Å. He suggests that these are the doublets of the isotopes of lithium, Li^6 and Li^7, although the intensity relations between them are by no means in accordance with this view unless a new theory is adopted. He proposes that, from these displacements and the displacements in the case of lead, the isotope displacements can be very closely obtained by multiplying the displacement calculable on the Bohr theory by the atomic number of the respective elements. In a later paper [36] on the absorption of λ 5460·97 by luminous mercury vapour, he describes satellites which he considers are due to the isotopes of mercury and quotes displacements agreeing with the empirical rule given above, but here again the intensity relations are not satisfactory. Merton, [37] recently commenting on these results, points out that the measurements of the enhanced lines of helium agree perfectly with the Bohr theory, and therefore definitely contradict McLennan's rule connecting atomic number with displacement. He also raises several exceedingly strong arguments against the possibility of the lithium doublets being in any way connected with the isotopic constitution of that element.

The difference between series spectra of isotopes is discussed gener-

[34] Proc. Roy. Soc., 1921, [A], 100, 84; A., 1921, ii, 611.

[35] Ibid., 1922, [A], 101, 342; A., ii, 541.

[36] J. C. McLennan, D. S. Ainslie, and (Miss) F. M. Cale, Proc. Roy. Soc., 1922, [A], 102, 33; A., ii, 728.

[37] Nature, 1922, 110, 632; A., ii, 803.

ally by Ehrenfest,[38] Bohr,[39] and Nicholson.[40]   Ehrenfest maintains that the ordinary Bohr formula, $\nu_2 : \nu_1 = M_2/M_2 + m : M_1/M_1 + m$, where M_1, M_2, and m are respectively the masses of the nuclei of the isotopes, and of the electron, and ν_1 and ν_2 the frequencies of the corresponding lines, cannot be true in general   Bohr admits that the effect of the mass of the nucleus on the spectrum of an atom containing more than one electron is a complex problem; not only may the mass effect disappear completely, but also may be different from that calculated for an atom with one electron. Nicholson points out that the large separation observed by McLennan in lithium cannot be explained by the quantum theory, and suggests that the new series may be a combination series or a spark series.

Band Spectra.—The wave-lengths of the higher members of the band spectrum of uranium lead and ordinary lead have been compared by Grebe and Konen.[41]   The chosen wave-lengths lie between 4257·690 and 4281·458 Å.U. Measurements of eighteen lines show that the wave-length of the line corresponding with uranium lead is on the average 0·055 Å.U. shorter than that for ordinary lead.   This figure agrees so far as its order is concerned with the assumption that the diatomic molecules are the carriers of the band spectrum.

Infra-red Spectra.—The extreme smallness of the isotope shift expected in the spectra discussed above is due to the fact that one unit of the vibrating system is the electron itself, the mass of which is extremely small compared with that of the other unit, the nucleus.   Very much larger effects are to be expected where two nuclei are concerned.   Loomis [42] shows that the doubling of the absorption bands in the infra-red spectrum of hydrogen chloride, first observed by Imes, can be explained on this view and gives a very satisfactory confirmation of the isotopic nature of chlorine. The frequencies of the doublets due to isotopes should be approximately proportional to $\sqrt{(m_1 + m_2)/m_1 m_2}$, where m_1 is the mass of the hydrogen nucleus and m_2 the mass of the charged halogen atom; hence the band lines should differ by 1/1330. The average interval measured was 14 Å.U. or 4·5 wave numbers, which agrees with the calculated value of 4·3 wave numbers.   Hydrogen fluoride does not show this effect, and in the case of hydrogen bromide the computed separations are too small to be observed as yet.

[38] *Nature*, 1922, **109**, 745; A., ii, 598.

[39] *Ibid.*, 746; A., ii, 598.

[40] *Ibid.*, 1922, **110**, 37; A., ii, 599.

[41] *Physikal. Z.*, 1921, **22**, 546; A., ii 4.

[42] *Astrophys. J.*, 1920, **52**, 248.

Separation of Isotopes.

Much work on the artificial separation of isotopes has been performed during the past two years, but nevertheless success has only been achieved in the case of two elements, mercury and chlorine. The work of Brönsted and Hevesy on the former [43] is particularly convincing both on account of the beauty and simplicity of the method used and the remarkable fidelity with which the results follow the theory, also fortunately simple. They found that if mercury is distilled at so low a pressure that molecules escaping from the surface of the liquid never return, and if at the same time the rate of distillation is kept down to a point at which the mixing of the liquid by self-diffusion is practically perfect, then the molecules of the different isotopes distil at rates inversely proportional to the square roots of their masses. In consequence, the lighter isotopes tend to increase in the first fractions and the heavier ones in the last residues of the distillation process. In their final work, 2700 c.c. of mercury were fractionated systematically to about 1/100,000 of the original volume in each direction. The density of the original mercury being taken as unity, the lighter fraction (0·2 c.c.) had a density 0·99974, and the heavier (0·3 c.c.) 1·00023. This corresponds with a difference of 0·1 of a unit in atomic weight. Using the same method with a solution of hydrochloric acid, they were later able to obtain evidence of a separation corresponding with 0·024 of a unit in the atomic weight of chlorine. [44] Egerton [45] announces a partial separation of the isotopes of zinc by the same method.

A change of about 0·05 of a unit has been achieved by Harkins [46] and Anson Hayes, [47] who used a method of diffusion through pipe-clay similar to that originally used in the separation of the isotopes of neon. [48] The system of diffusion was elaborate, large quantities of material were employed, and the experiments occupied a long period. In this and in a later communication, [49] the theory of the resolution of isotopic mixtures by diffusion is discussed at some length and it is suggested that slight separation of isotopes occurs during ordinary distillation under reduced pressure. Mulliken [50] gives a very complete theory of the separation of isotopes by thermal

[43] *Z. physikal. Chem.*, 1921, **99**, 189; *Phil. Mag.*, 1922, [vi], **43**, 31; *A.*, ii, 140.

[44] *Nature*, 1921, **107**, 619; *A.*, ii, 280.

[45] *Ibid.*, 1922, **110**, 773; *A.*, 1923, ii, 28.

[46] *J. Amer. Chem. Soc.*, 1921, **43**, 1803; *A.*, ii, 140.

[47] *Ibid.*

[48] *A.*, 1919, ii, 209.

[49] R. S. Mulliken and W. D. Harkins, *ibid.*, 1922, **44**, 37; *A.*, ii, 295.

[50] *Ibid.*, 1033; *A.*, ii, 492.

diffusion and by centrifuging, and shows that the latter method is likely to be of more value in the case of isotopes of high atomic weight. A special method, named evaporative centrifuging, is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fractions being drawn off very gradually at low pressure from the centre of the apparatus. It is suggested that this method ought to yield a separation ten to fifteen times as great in one operation as would diffusion or evaporation. He also discusses the possibility of separating liquid isotopes by centrifuging, a method which has been considered by Poole.[51] An attempt to test this theory in the case of mercury proved unsuccessful, and its failure is attributed to slight vibration of the centrifuge.

Kohlweiler [52] still maintains the opinion that he has separated the isotopes of iodine, although the existence of these is contrary to the direct evidence of the mass-spectrograph. He ascribes his results to isotopes present in too small quantities to be detected by that apparatus. If this is the case, it is very difficult to understand how it could be possible to obtain the relatively enormous shift—$0·88$ of a unit—claimed, by any diffusion method.

Perhaps the most surprising report is that from Dublin claiming the separation of lead isotopes by chemical means.[53] Lead chloride was prepared from a mixture of ordinary lead and thorium lead, and the reaction represented by the equation $2PbCl_2 + 4MgRX = R_4Pb + 2MgCl_2 + 2MgX_2 + Pb$ carried out. The lead tetraethyl and metallic lead constitute the fractions which are used separately in a repetition of the process. By two repetitions a separation indicated by relative atomic weights $207·1$ and $207·4$ is claimed. This result will need very strong confirmation before it is generally accepted, for the method is founded on an observation of Hoffmann and Wolf [54] in 1907 that a large separation of lead from radium-D could be effected by a single reaction with magnesium phenyl bromide. This statement was in direct contradiction to all the work of the most careful experimenters at that date, it has never been confirmed since, and is regarded by the most competent authorities in radioactivity to-day as probably erroneous.

Other possible methods of separation have been put forward. Skaupy [55] suggests that the differential effect of electronic impacts

[51] *Phil. Mag.*, 1921, [vi], **41**, 818; *A.*, 1921, ii, 403.
[52] *Z. physikal. Chem.*, 1922, **101**, 218; *A.*, ii, 497.
[53] T. Dillon, R. Clarke, and V. M. Hinchy, *Sci. Proc. Royal Dublin Soc.*, 1922, **17**, 53; *A.*, ii, 710.
[54] *Ber.*, 1907, **40**, 2425.
[55] *Z. Physik*, 1920, **2**, 213; *A.*, 1921, ii, 154.

in an electric discharge would give a separation of isotopes of the rare gases. Ludlam [56] describes experiments carried out to test a method of separation of the isotopes of chlorine based on a suggestion made by Sir J. J. Thomson that the number of impacts per second of the molecules of a gas on a surface will be in the inverse square root of their mass. Hydrogen chloride at a pressure of a few centimetres of mercury was passed over (a) a water surface, and (b) ammonia gas, and a small fraction allowed to remain uncombined. No change in molecular weight was observed after either process. An ingenious photochemical process has also been investigated.[57] If chlorine consists essentially of a mixture of three parts of Cl^{35} and one part of Cl^{37}, the molecules should be present in the proportions $Cl^{35}_2 : Cl^{35}Cl^{37} : Cl^{37}_2 = 9 : 6 : 1$. If light which has passed through a column of such chlorine enters a mixture of chlorine and hydrogen, the initial reaction should use up the three types of molecules in the proportions $1 : 10^9 : 10^{24}$, and the hydrogen chloride formed should be almost entirely HCl^{37}. The experimental results, however, of applying this method were entirely negative.

In conclusion, it may be pointed out that the actual numerical results achieved by lengthy and laborious operations in the few successful attempts indicate very clearly that unless some entirely new means of attack is devised no serious practical disturbance of the constants of chemical combination need be anticipated in the immediate future.

Artificial Disintegration of the Lighter Elements by the Collision of Swift α-Particles.

The remarkable results in this field obtained by Rutherford and Chadwick during the year 1921 have already been reported,[58] and a complete account of their work up to February 1922 will be found in Sir Ernest Rutherford's lecture before the Chemical Society.[59] In a more recent publication,[60] these results have been confirmed and extended. The nature of the particles ejected from the various elements during the bombardment by swift α-particles has been directly investigated by measuring their deflexions in a magnetic field. The results show that in the cases of aluminium, phosphorus, and fluorine the particle ejected is a single positively

[56] *Proc. Camb. Phil. Soc.*, 1922, **21**, 45; *A.*, ii, 497.

[57] H. Hartley, A. O. Ponder, E. J. Bowen, and T. R. Merton, *Phil. Mag.*, 1922, [vi], **43**, 430; *A.*, ii, 280.

[58] *Ann. Rep.*, 1921, **18**, 31.

[59] T., 1922, **121**, 400.

[60] Sir E. Rutherford and J. Chadwick, *Phil. Mag.*, 1922, [vi], **44**, 417; *A.*, ii, 682.

charged hydrogen nucleus, which is now regarded as being identical with the ultimate atom of positive electricity or proton. The same is also probably true of boron and sodium. The ranges of the protons ejected, in the forward and backward directions, from nitrogen, aluminium, boron, fluorine, sodium, and phosphorus have been more accurately determined. In all cases, the protons were ejected in all directions, and the maximum range in the backward direction was less than in the forward direction. The maximum ranges, in cm. of air, of the ejected protons, in the forward and backward directions, respectively, were found to be : boron, 58 and 38; nitrogen, 40 and 18; fluorine, 65 and 48; sodium, 58 and 36; aluminium, 90 and 67; and phosphorus, 65 and 49. Only in the case of nitrogen was the maximum range in the backward direction much less than that of the protons produced by the bombardment of hydrogen itself. No protons of range greater than 30 cm. of air, in a forward direction, were ejected from either lithium or glucinum, and there is no evidence of the ejection of long-range protons from magnesium, silicon, or chlorine. It is a very remarkable thing that of the series of elements from hydrogen to potassium so far examined the active elements (those from which high-speed protons can be ejected) are odd-numbered in the order of atomic number in sequence 5, 7, 9, 11, 13, 15. The atomic masses of these active elements are all expressed by $4n + a$, where n is a whole number and $a = 3$ for all except nitrogen and the lighter isotope of boron, for which $a = 2$. With the one exception of boron, all are simple elements.

It is evident from these results that the nuclei of even light elements are very complex structures. The effects mentioned above are best explained by the view that the fragile nuclei of the active elements have a different proton-electron structure from those not exhibiting disintegration, and that their fragility is due to the presence of what may be called " planetary " protons less firmly bound than their fellows and probably rotating in orbits of nuclear dimensions. The fact that chlorine and the heavier elements do not break up may be ascribed to their nuclear charge being so high that the α-particle never makes a close enough collision to effect disintegration. Disintegration is clearly akin to ionisation, since in each case a unit electric charge is torn violently away from the atom, but beyond this the parallel ceases. In the case of ionisation the field of force round the atom is of a sign which attracts the electron dislodged, or any other electron, and extends indefinitely in all directions, so that the atom is sure to regain its neutral form very rapidly. On the other hand, in disintegration, any field of force tending to regain the proton lost is confined to nuclear dimensions

and in addition is surrounded indefinitely in all directions by a field of force repelling such a positive charge. The effect of ionisation is therefore transitory, whilst that of disintegration is permanent, and it is not unreasonable to speculate that when a proton is dislodged from an atom of sodium (Na^{23}) there results an atom of neon (Ne^{22}) which, as soon as it has lost its excess electron, will be indistinguishable in any way from any other atom of Ne^{22}. Even if the actual effect is not so simple as this, there can be no doubt that alchemical transmutation has been achieved. An attempt made by Wyckoff [61] to effect transmutation by bombardment of lithium salts by a stream of electrons, in the hope of introducing one or two into the nuclei of the lithium atoms, was unsuccessful. The claim put forward by Wendt and Irion [62] that tungsten is decomposed and partly transmuted into helium when, in the form of a fine wire, it is electrically deflagrated at a very high temperature, appears so excessively improbable that it may be safely left for further confirmation.

α-Rays.

The range of α-rays in solids and liquids has been measured by Traubenberg. In the first case,[63] a small-angled wedge of the material was arranged with its lower face parallel to, and at a distance of a few millimetres from, a plane surface activated by means of radium-C. The upper face of the wedge was in contact with a zinc sulphide screen. The range of the α-rays in the solid was determined by observing the distance of the line of demarcation between the light and dark regions of the screen from the angle of the wedge. Correction was made for the thickness of air traversed. β-Radiation was eliminated by a powerful magnetic field. The following results were obtained for the respective ranges, expressed in 10^{-4} cm., in the various elements stated : lithium, 129·1; magnesium, 57·8; aluminium, 40·6; calcium, 78·8; iron, 18·7; nickel, 18·4; copper, 18·3; zinc, 22·8; silver, 19·2; cadmium, 24·2; tin, 29·4; platinum, 12·8; gold, 14·0; thallium, 23·3; lead, 24·1. These results can be correlated by a formula, but helium and lithium do not satisfy this relation; this discrepancy is ascribed to the production of secondary α-radiation.

In the case of liquids,[64] the range was measured by immersing the activated plate in the liquid and lowering the screen towards it until it just fluoresced; the thickness of the liquid was then

[61] *Science*, 1922, **55**, 130; *A.*, ii, 642.

[62] *J. Amer. Chem. Soc.*, 1922, **44**, 1887; *A.*, ii, 773.

[63] *Z. Physik*, 1920, **2**, 268; *A.*, 1921, ii, 148.

[64] H. R. von Traubenberg and K. Philipp, *Physikal. Z.*, 1921, **22**, 587; *A.*, ii, 12.

measured with a horizontal microscope. The range in water was found to be 60μ. Gases were investigated by passing the beam of rays parallel to the sides of a glass wedge, containing the gas, and placing in their path a screen at a small angle with the horizontal. As in the case of solids, the range was deduced from the boundary of dark and light on the screen. They found that the stopping power of gases varies as the square root of the atomic number, but is not strictly additive in the case of compounds.

The luminous path of α-rays in crystals has been observed by Geiger and Werner.[65] A thin, highly polished section of willemite was arranged in the field of a microscope so that the α-rays of polonium should strike it at a small angle. Luminous lines, 0·03 mm. long, were seen. These represent the path of the α-ray in the crystal and show that the number of centres is extremely large, and in the case of a perfect crystal sufficient to ensure a scintillation for every α-particle hitting the crystal.

Some exceedingly important observations on the collisions between α-particles and hydrogen nuclei have been made by Chadwick and Bieler.[66] The angular distribution of these nuclei, or protons, projected by α-particles of mean range 6·6 cm., has been determined up to an angle of 66°. The distribution for α-rays of mean ranges 8·2, 4·3, and 2·9 cm. has been obtained over a smaller range of angle. The number of protons projected within these small angles by α-rays of high velocity is greatly in excess of that given by forces varying as the inverse square of the distance between the centres of the two nuclei. The manner in which the number of protons projected varies with the velocity of the rays has been observed over a wide range. For rays of high velocity this variation is in the opposite direction to that given by the inverse square law; for those of range less than 2 cm. the collision relation is about the same as that expected from the inverse square law. The experimental collision relation is compared with those calculated by Darwin for various models of the particle, and the conclusion is drawn that the α-particle behaves in these collisions as an elastic oblate spheroid of semi-axes about 8×10^{-13} and 4×10^{-13} cm., moving in the direction of its minor axis. Outside this surface the force varies approximately as the inverse square of the distance from the centre of the spheroid.

Slater [67] has investigated the hard γ-radiation which is emitted when α-particles from radium emanation impinge on metals such as lead and tin. The radiation differs but little with change of

[65] *Z. Physik*, 1921, **8**, 191; *A.*, ii, 183.
[66] *Phil. Mag.*, 1921, [vi], **42**, 923; *A.*, ii, 12.
[67] *Ibid.*, 904; *A.*, ii, 13.

atomic number. The absorption coefficients in lead are 1.8^{-1} cm. for lead and 2.1^{-1} cm. for tin. The intensity obtained is small, and is about 50 per cent. greater for lead than for tin. It appears to be emitted fairly uniformly in all directions, but differs in all other respects from the characteristic radiations, and is probably emitted from the nuclei of the atoms in the radiator after direct collision with the α-particles. Shenstone [68] has attempted to detect the induced radioactivity resulting from α-ray bombardment. He shows that the violent dismemberment of a molecule by an α-particle does not give rise to unstable nuclei, capable of emitting mass particles of a range greater than 2.0 mm. Also no cumulative effect is observable after a heavy bombardment by the α-particles. These negative results do not preclude the possibility of disintegrations taking place which involve the emission of β-particles or γ-radiation.

The velocity of α-rays from polonium has been measured directly by Mlle Irene Curie [69] by means of a magnetic deviation method. A value of 1.593×10^9 cm. per second is obtained and the ratio of the emission velocities of the α-rays of polonium compared with those of radium-C is accordingly 0.829, which is in excellent agreement with the ratio 0.826 obtained from the cube roots of their penetrating powers. An interesting point is raised by Henderson [70] in a communication entitled " α-Particles as Detonators." If it is considered that when an α-particle passes through matter the matter in its proximity is momentarily raised to a high temperature, the detonation of certain unstable substances would be expected to take place on exposure to the action of these particles. Air-dried nitrogen iodide is detonated in this way. The detonation is not caused by the first α-particle which happens to strike the substance, but appears to be a probability effect. The same investigator [71] has measured the ionisation curves of α-particles from radium-C, thorium-C_1, and thorium-C_2 in air, particular attention being directed to the end portions. The greater part of each curve is approximately a straight line. The gradual flattening of the curve at the end of the range can be accounted for by small variations in the ranges of individual α-particles. He suggests that an extrapolated range is more suitable than the usual definition. The extrapolated range in air at 0° is 6.592 cm. for radium-C, 4.529 cm. for thorium-C_1, and 8.167 cm. for thorium-C_2.

[68] *Phil. Mag.*, 1922, [vi], **43**, 938; *A.*, ii, 377.
[69] *Compt. rend.*, 1922, **175**, 220; *A.*, ii, 666.
[70] *Nature*, 1922, **109**, 749; *A.*, ii, 606.
[71] *Phil. Mag.*, 1921, [vi], *42*, 538; *A.*, 1921, ii, 617.

The Scattering of β-Rays.

Geiger and Bothe [72] have measured the scattering of β-rays by thin metal sheets (a) in the regions of small scattering angle ($\phi = 15°$ or less) and (b) in the regions of large scattering angle ($\phi = 60°$ or more). They show that there is a fundamental difference between the two types of scattering. In the region of smaller angles, the observed angle is produced by the superposition of many individual small scattering angles through which the β-ray is bent as it passes the individual atoms (multiple scattering), whilst in the region of large angles the superposition plays a subordinate rôle; each scattering angle is produced by a single collision when the path of the electron lies very close to the nucleus of the atom collided with (individual scattering). In the case of rays from radium-($B + C$), they show that for the very thinnest layers the scattering is less than that demanded by the square root law, but that for thicker layers this law is confirmed.

·The same phenomenon has been very completely investigated by Crowther and Schonland.[73] A source of radium emanation of an initial activity equivalent to that of 45 mg. of radium was employed and the scattering of the β-rays caused by foils of gold, silver, copper, aluminium, and carbon was measured over ranges of both large and small angles. In the experiments on the relation between the transmitted radiation and the thickness of the scattering material, they conclude that this is a linear one for thin foils. If t_m is the thickness of material sufficient to cut down the radiation to one-half its initial intensity, their results may be summarised by stating that, for light elements such as carbon and aluminium, the scattering as measured by $\phi/\sqrt{t_m}$ is independent of ϕ over the whole range of the angles investigated (4° to 18°), but has a value which is nearly twice that to be expected on the current theories of the effect. On the other hand, for heavy elements like gold or platinum, the scattering for very small values of ϕ approximates closely to that to be expected from theoretical considerations, but increases rapidly with the angle, until for angles of 18° it is in agreement with the larger scattering shown by the lighter elements at all angles measured.

Their method of viewing the data strongly suggests that some change is required in the present theory when the distance between the path of the β-particle and the deflecting particle is less than a certain critical value.

Glasson [74] has tabulated values of the atomic absorption,

[72] Physikal. Z., 1921, 22, 585; A., ii, 13.
[73] Proc. Roy. Soc., 1922, [A], 100, 526.
[74] Phil. Mag., 1922, [vi], 43, 393; A., ii, 183.

$a = \alpha A/D$, and the atomic scattering, $b = \beta A/D$ (where A is the atomic weight, D the density, and α and β are the coefficients of absorption and of scattering, respectively, for β-rays) of the elements, and has discovered two interesting relations. He finds that the values of a are approximately constant for elements in the same period of the periodic system. Thus for Mg,Al, $a = 89$; for Fe,Co,Ni,Cu,Zn, $a = 172$—196; for Pd,Ag,Sn, $a = 260$—268; and for Pt,Pb,Au,Bi, $a = 348$—372. These figures are in the ratio $1:2:3:4$, so that it seems likely that the value of a is a periodic function of the atomic number. The value of b increases with atomic number and is approximately represented by the expression $b = 0.36 \times N^{2.09}$.

β-Rays, γ-Rays, and the Structure of the Nucleus.

The comparative lack of experimental data connected with the structure of the nucleus gives a very free field to speculative theory on that subject. The nucleus model put forward by Meitner[75] has been discussed by Neuberger, Valeras, and its originator in a number of papers of a speculative and controversial nature.[76] Other types of models are put forward by Gehrcke,[77] Chwolson,[78] and Stewart.[79]

Ellis [80] has examined the magnetic spectrum of the β-rays excited by the γ-rays of radium-B in uranium, lead, platinum, tungsten, and barium. He shows that the main lines are formed by electrons ejected from the K-rings of these elements by definite γ-rays, each type of γ-ray being characterised by a certain energy. In a later paper,[81] he develops a method, based on the quantum theory, by which the wave-length of γ-rays, too short to be measured by the crystal method, can be determined, and applies this to the cases of the γ-rays of radium-B, radium-C, and thorium-D. The method consists in the determination of the energies of the different lines in the natural β-ray spectrum of the element in question, and the energy of the corresponding line in the excited spectra of substances of neighbouring atomic number. The numerical results obtained support the view that the γ-rays are emitted from the nucleus. They also suggest that the quantum theory is applicable to the nucleus, and a part, at least, of the structure of the nucleus is expressible in terms of stationary states.

[75] Z. Physik, 1921, **4**, 146; A., ii, 293.
[76] A., ii, 107, 183, 185, 416, 702, 732, 733.
[77] A., 1921, ii, 323.
[78] A., ii, 209.
[79] A., ii, 277.
[80] Proc. Roy. Soc., 1921, [A], **99**, 261; A., 1921, ii, 422.
[81] C. D. Ellis, ibid., 1922, [A], **101**, 1; A., ii, 339.

Meitner,[82] on the other hand, although admitting that the origin of the γ-rays is the nucleus itself, gives an entirely different explanation of Ellis's results on the basis of her nucleus model, developed by the application of the quantum theory by Smekal.[83] The Meitner-Smekal theory supposes that the primary cause of γ-rays are β-rays of definite energies, and on it the well-known continuous β-ray spectrum must be considered to be entirely adventitious and produced under experimental conditions by some such agency as scattering. Ellis's explanation, which is more in accord with the older work of Chadwick,[84] is that the disintegration electrons form the continuous spectrum. The homogeneous groups are considered to be entirely secondary in origin and due to the conversion of γ-rays in the electronic structure of the radioactive atom, these γ-rays being emitted from the nucleus during the disintegration.[85] Chadwick and Ellis [86] have made a preliminary measurement of the intensity distribution in β-ray spectra of radium-B and radium-C, under conditions which enabled scattering effects to be eliminated or corrected for. Their results show that in each case by far the greater part of the intensity is in the continuous spectrum, a fact exceedingly difficult to explain on the Meitner-Smekal theory, and are generally in strong support of that put forward by Ellis.

The work on β-rays caused by γ-rays is still in progress and has already raised points of very great interest. It suggests that the origin of some of the electrons forming the β-rays must be inside the K-ring and therefore within the nucleus itself, and that these electrons have energies corresponding with definite quantum levels, just as the ordinary planetary electrons outside are known to have. Now the effect of an isotopic difference in the structure of nuclei may be expected to have an enormously greater effect on β-ray spectra caused by nuclear electrons than it would have on X-ray or ordinary light spectra caused by planetary electrons. Multiple lines observed already give evidence that some of the heavy elements examined are mixtures of isotopes, but, unfortunately, none of these has yet been analysed by the mass-spectrograph. It is also clear that if an electron is dislodged from the nucleus by the agency of a γ-ray produced in the nucleus itself, it is just possible that the same effect could be produced, and transmutation effected, by a γ-ray from an exterior source. Assuming that the emission of

[82] Z. Physik, 1922, 9, 131; A., ii, 416.
[83] Ibid., 1922, 10, 275.
[84] Verh. deut. Physikal. Ges., 1914, 16, 383.
[85] C. D. Ellis, Proc. Camb. Phil. Soc., 1922, 21, 121; A., ii, 466.
[86] Ibid., p. 274.

γ-rays may precede the process of disintegration, Hevesy [87] shows that if the nucleus could take up the energy of a γ-ray from an external source it should change its stability and therefore its rate of disintegration. He has experimented with uranium in radio-active equilibrium with uranium-X, and with radium-D in equilibrium with radium-E, but has failed to detect a measurable change in the β-radiation in either case.

Thorium.

Long-range Particles from Thorium-C.—In the disintegration of thorium-C a small number of particles with the long range of 11·3 cm. are expelled.[88] As there was a possibility that these had originated by collisions of the α-particles with the oxygen of the mica absorbing screen, the phenomena were re-examined with screens of aluminium as well as mica.[89] The same results were obtained in both cases. The ratio of the total number of particles with ranges exceeding 8·6 cm. to the total number of α-particles (ranges 5·0 and 8·6 cm.) is 1 to 11,000. At least 90 per cent. of the long-range particles originate in the active deposit. Measurement of the deflexion of these particles in a magnetic field showed that they were ordinary α-particles of mass 4. There is no information as to their source. It may be that thorium-C may break up in two ways with the emission of rays of ranges 8·6 and 11·3 cm., or that 1 in 11,000 of the atoms of thorium-C breaks up directly with emission of these very swift α-particles. The resulting product would have an atomic number 81, and would be an isotope of thallium with atomic weight 208. The amount of this thallium found in thorium minerals should be about 0·00004 per cent.

The number and the range of the recoil atoms of thorium-C and thorium-C' have been investigated by Kolhorster.[90] Aluminium foil, activated by a mesothorium preparation, was used as a source of the radiation. It is concluded that a recoil atom results from each atom of thorium-C and thorium-C' transformed by the emission of an α-ray. The average ranges found in hydrogen were 0·55 mm. and 0·96 mm., respectively, corresponding with ranges of 0·129 mm. and 0·224 mm. in air at 15° and 760 mm.

A determination of the number of α-particles per second emitted by thorium-C of known γ-ray activity has been made by Shenstone and Schlundt.[91] The α-particles were counted by the wheel method

[87] *Nature,* 1922, **110,** 216; *A.,* ii, 608.

[88] Sir E. Rutherford, *Phil. Mag.,* 1921, [vi], **41,** 570; *A.,* 1921, ii, 293.

[89] A. B. Wood, *ibid.,* p. 575; *A.,* 1921, ii, 294.

[90] *Z. Physik,* 1920, **2,** 257; *A.,* 1921, ii, 149.

[91] *Phil. Mag.,* 1922, [vi], **43,** 1038; *A.,* ii, 417.

devised by Rutherford, and accurate γ-ray measurements were made at the same time as the counts. Counts made with thorium-C and radium-C showed that the ratio of their α-ray activities for equal γ-ray activities is not independent of the thickness of the wall of the γ-ray electroscope.

The volatility of a radioactive product, deposited on metal, has been examined in the case of thorium-B and thorium-C, deposited on gold, platinum, and palladium.[92] A discontinuity at about 760° is put down to the occurrence of thorium-C oxide stable at this temperature.

Strong[93] has made a careful series of fractionations of a mixture containing radium and mesothorium obtained during the process of extraction from barium compounds. No separation whatever could be detected, from which it is concluded that radium and mesothorium are true isotopes.

Uranium and Actinium

Adams[94] points out that Piccard's assumption[95] that the actinium series is derived neither from uranium-I nor from uranium-II does not require the identity of the periods of the first and the third. A hypothetical isotope of protoactinium (ekatantalum or uranium-Z) is assumed as the parent of actinuranium by a β-ray transformation. He assigns to this element an atomic weight 235, corresponding with protoactinium 231, actinium 227, and actinium lead 207, and points out that the last value agrees well with Hönig-schmid's value of 206·05 for the atomic weight of uranium lead containing about 3 per cent. of actinium lead.

Meyer[96] calculates the half-life period of actinium to be about sixteen and a half years, and the transformation ratio of the actinium to the uranium family to be 4·2 per cent. Hahn and Meitner[97] consider this value to be 25 per cent. too high, and prefer their own value, $3 \pm 0·3$ per cent. They consider that Meyer's preparation probably contained 1—2 per cent. of ionium, which would explain the difference. The same workers,[98] by separation of the protoactinium from uranium of approximately known age and measurement of its activity in comparison with that of uranium, have been able to estimate its half-life period as about 12,000 years. This value is the result of three concordant experiments and is

[92] S. Loria, *Krakauer Anzeiger*, 1917, 260; *A.*, 1921, ii, 294.

[93] *J. Amer. Chem. Soc.*, 1921, **43**, 440; *A.*, 1921, ii, 294.

[94] *Ibid.*, 1920, **42**, 2205; *A.*, 1921, ii, 8.

[95] *A.*, 1918, ii, 6.

[96] *Wien. Anzeiger*, 1920, 133; *A.*, 1921, ii, 8.

[97] *Z. Physik*, 1921, **8**, 202; *A.*, ii, 185.

[98] *Ber.*, 1921, **54**, [*B*], 69; *A.*, 1921, ii, 150.

to be regarded as the lower limit. It is thus possible to calculate the protoactinium content of uranium minerals, which is expressed by the figure 72 mg. of protoactinium to one ton of uranium; the corresponding figure for radium is 330 mg.

New Radioactive Substances in Uranium.—Hahn [99] describes a new radioactive substance present in ordinary uranium salts possessing the chemical properties of protoactinium. It emits $_,\beta$-radiations and has a half-life period of six to seven hours. The radiations are highly complex; within the limits examined, the halving thickness increases from 0·014 to 0·12 mm. of aluminium. Under the prescribed conditions, the intensity of radiation of the new substance is only about 0·25 per cent. of that of uranium-X (uranium-X_1 + uranium-X_2), obtained from the same quantity of uranium. The parent substance can only be uranium-X_1 or a new uranium-X_1 isotope of similar life period. In the former case, uranium-X_1 suffers a dual degradation of a type not yet observed. In the latter case, it is probable that a new uranium degradation series exists which has a small intensity of radiation and the individual members of which can be arranged as isotopes in the known uranium–radium series. Until the parentage of the new substance is definitely established, the author proposes to designate it " uranium-Z." Neuburger [1] suggests possible types of disintegration in the uranium–radium series to account for the occurrence of the new uranium-Z. Hahn,[2] however, rejects the transformations suggested by Neuburger as improbable.

Piccard and Stahel [3] have repeatedly measured the β-radiation of a quantity of uranium-X for a prolonged period. They show that in addition to the hard β-radiation of uranium-X, there is a soft radiation which with increasing age of the preparation decreases more and more slowly; this indicates the presence of a substance of longer life than uranium-X. They name this provisionally " uranium-V." It has a half-life period of about forty-eight days, its β-radiation is half absorbed by an aluminium sheet 0·0003 mm. thick, and it may be a member of the actinium series. Hahn [4] has determined the decrease in activity of a number of uranium-X preparations to test these observations, but has found no evidence of the existence of uranium-V.

<div align="right">F. W. ASTON.</div>

[99] *Ber.*, 1921, **54**, [*B*], 1131; *A.*, 1921, ii, 478.
[1] *Naturwiss.*, 1921, **9**, 235; *A.*, 1921, ii, 479.
[2] *Ibid.*, 236; *A.*, 1921, ii, 479.
[3] *Physikal. Z.*, 1922, **23**, 1; *A.*, ii, 185.
[4] *Ibid.*, 146; *A.*, ii, 340.

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